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(54) Abstract Title
Growing metal nitride crystals

(57) Crystals of metal nitrides (eg GaN, AlN, InN) are grown by feeding nitride crystal powders 106 and a liquid encapsulating material 105 into a cylinder 107 and heating 104 while pressurizing with a piston 103 and then allowing the nitride to solidify at normal temperature and pressure. The liquid encapsulating material may be B_2O_3, KCl, NaCl, $BaCl_2$ or $CaCl_2$. A seed crystal may be present in the nitride material.

FIG. 13
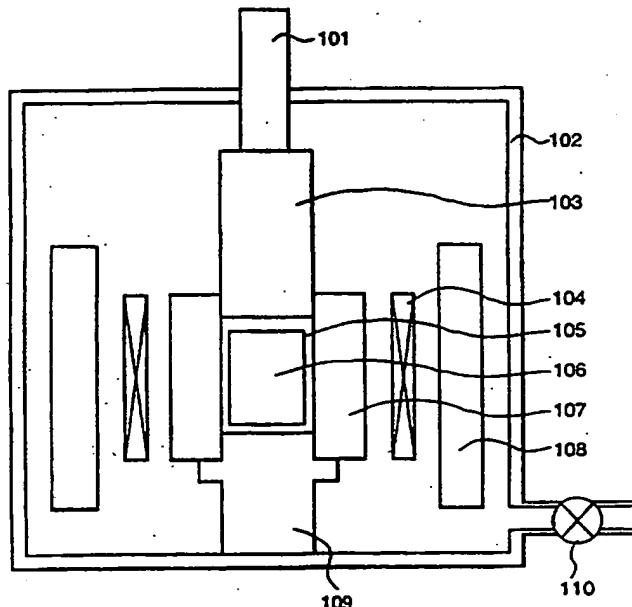
GB 2 333 521 A

FIG. 1

NH 3

5

TO EXHAUST GAS
TREATMENT EQUIPMENT

4

1

2

3

6

FIG. 2

FIG. 3

FIG. 4

PL INTENSITY (a.u.)

350   500   650

PL WAVE LENGTH

FIG. 5

PL INTENSITY (a.u.)

350   500   650

PL WAVE LENGTH

FIG. 6

FIG. 7

FIG. 8

NH₃ →

TO EXHAUST GAS
TREATMENT EQUIPMENT

FIG. 9

TO EXHAUST GAS
TREATMENT EQUIPMENT

NH 3

37

36

31

34

32

33

35

FIG. 10

PL INTENSITY (a.u.)

350   500   650

PL WAVE LENGTH

FIG. 12

PL INTENSITY (a.u.)

350   500   650

PL WAVE LENGTH

FIG. 11

TO EXHAUST GAS
TREATMENT EQUIPMENT

NH₃
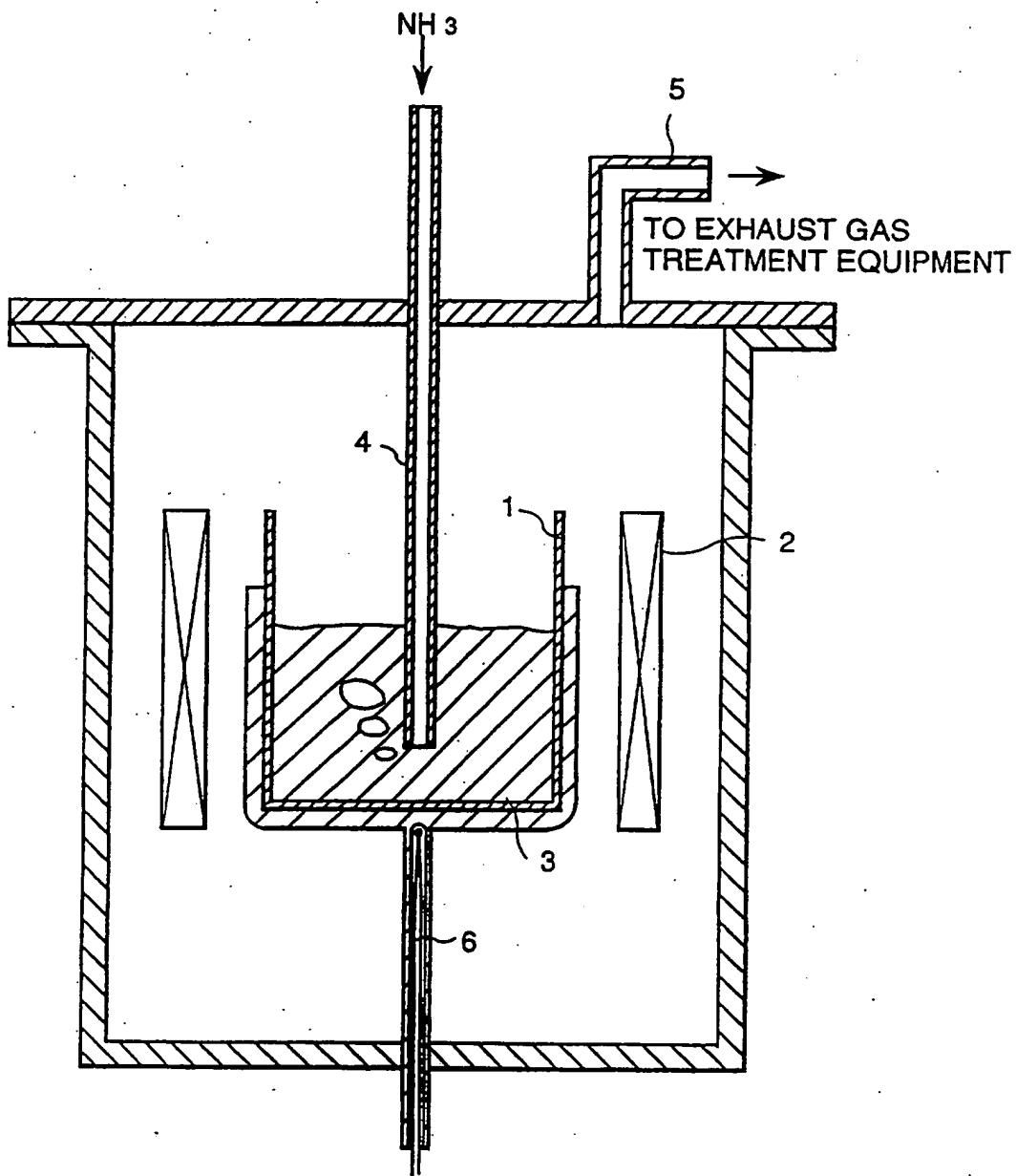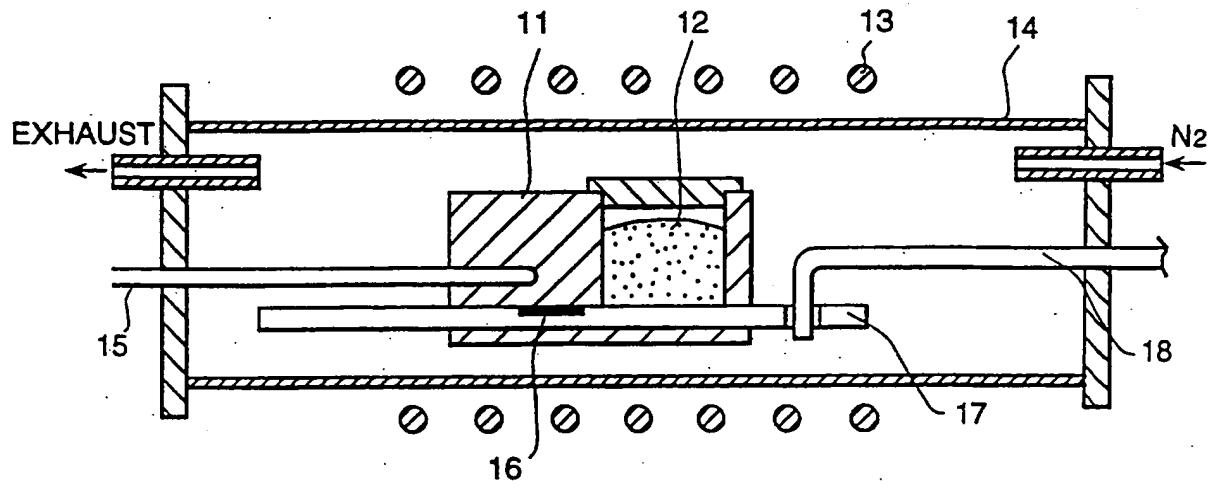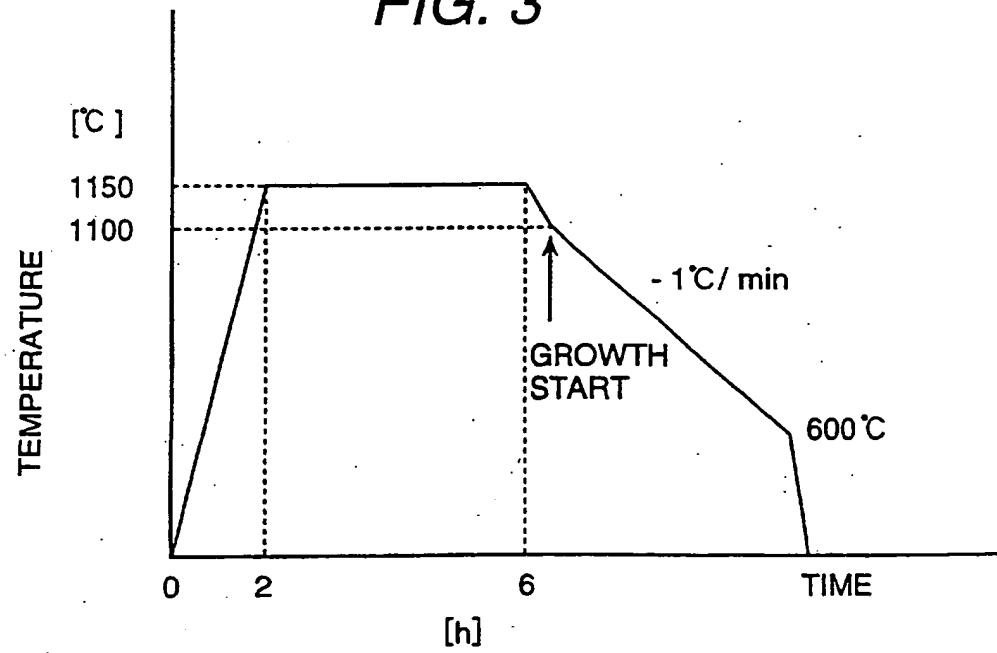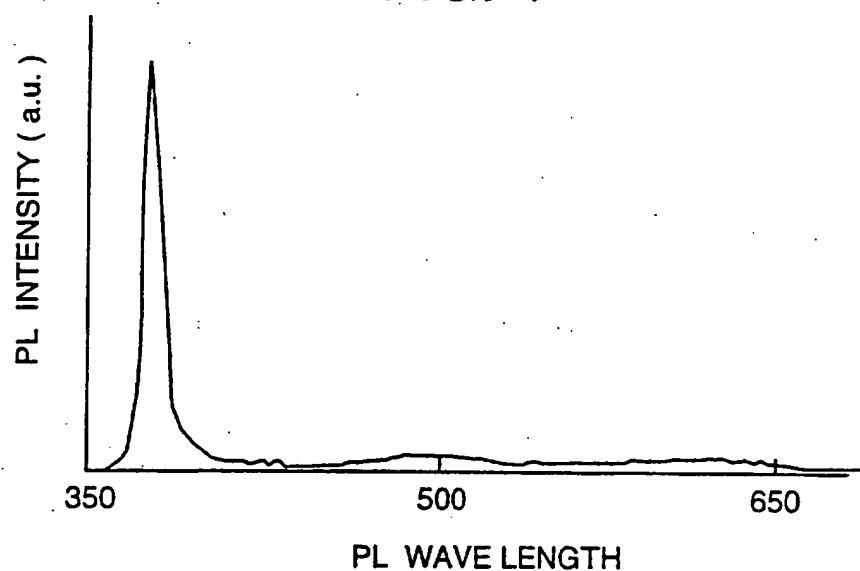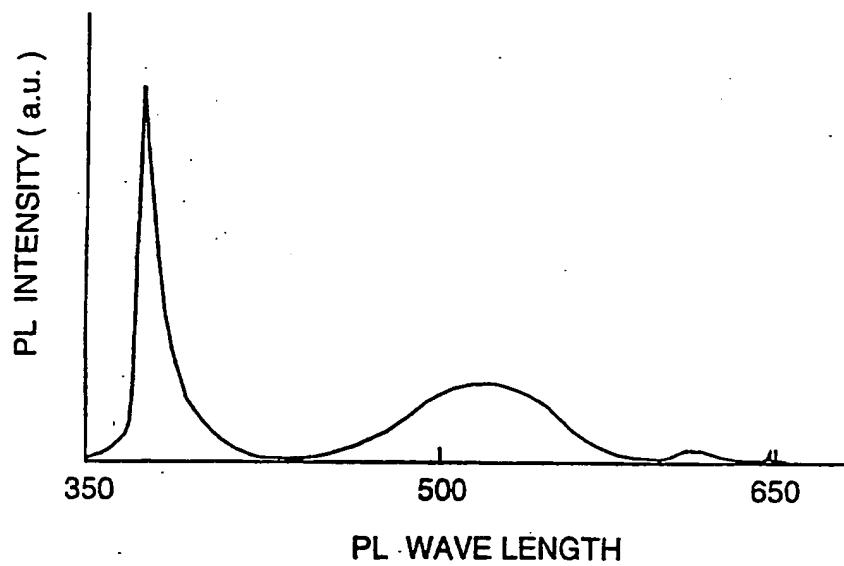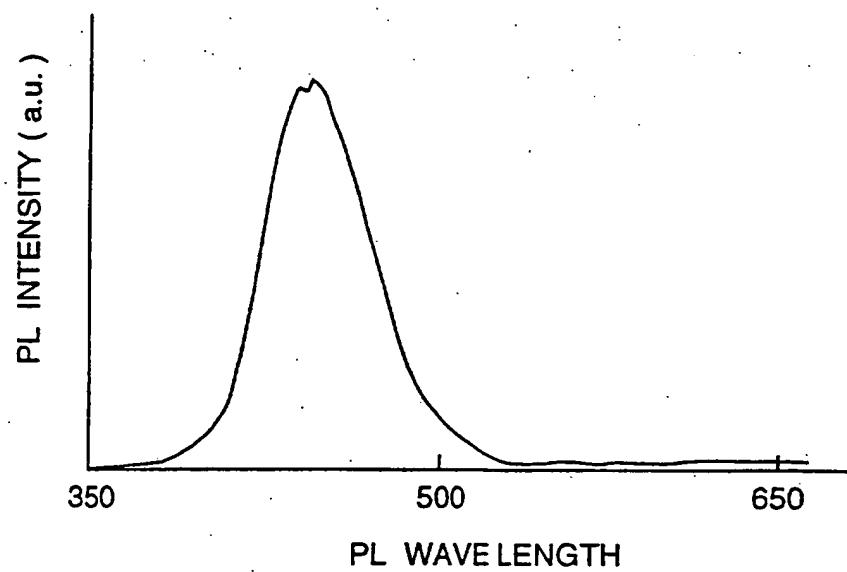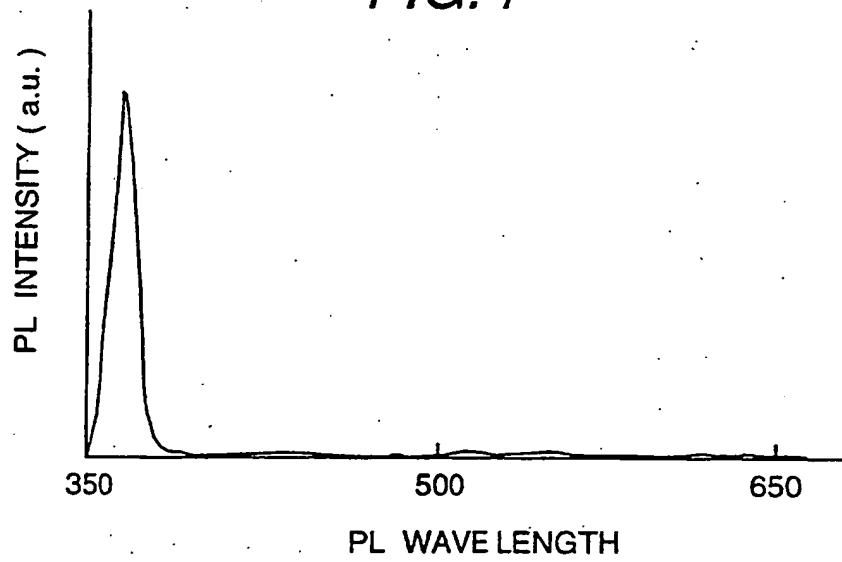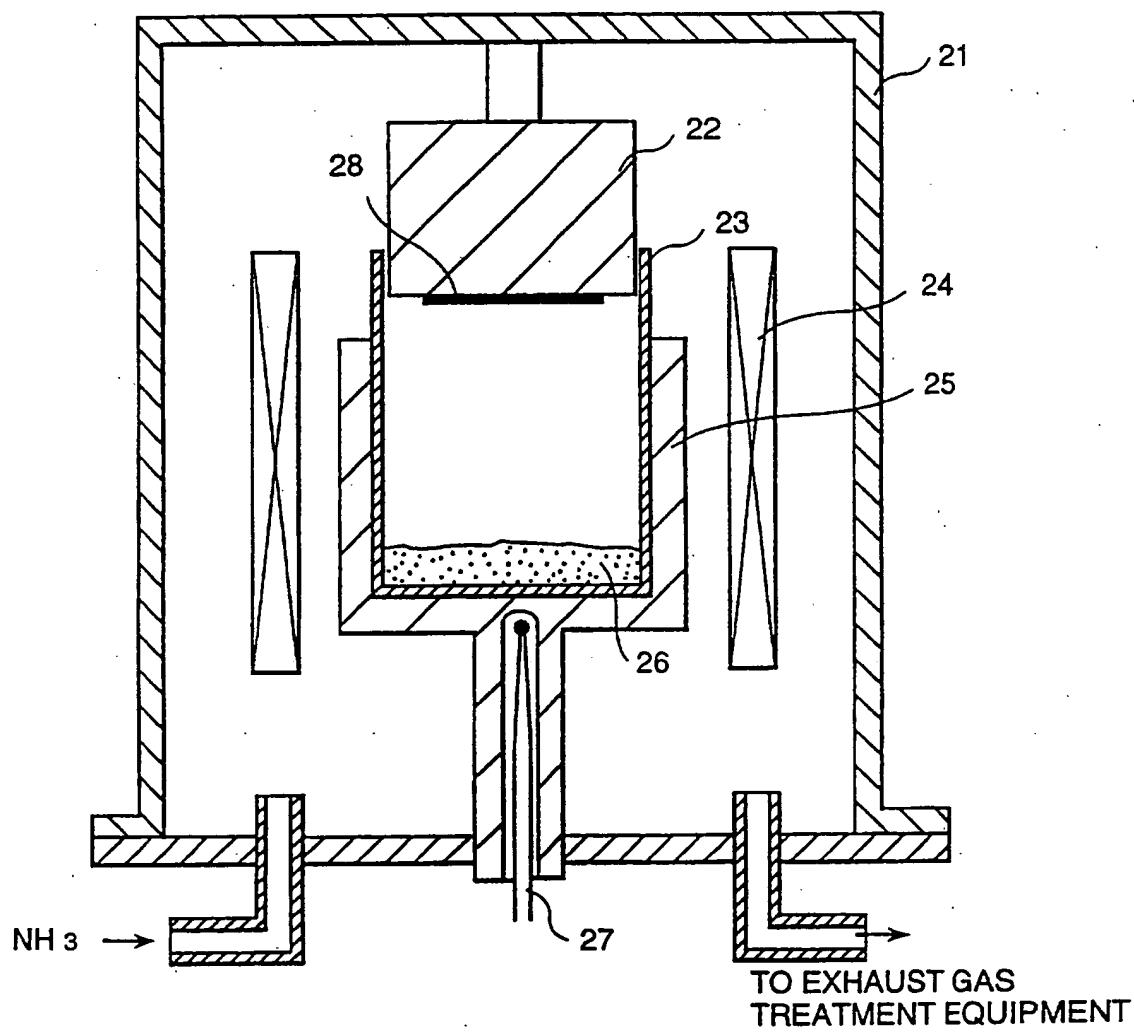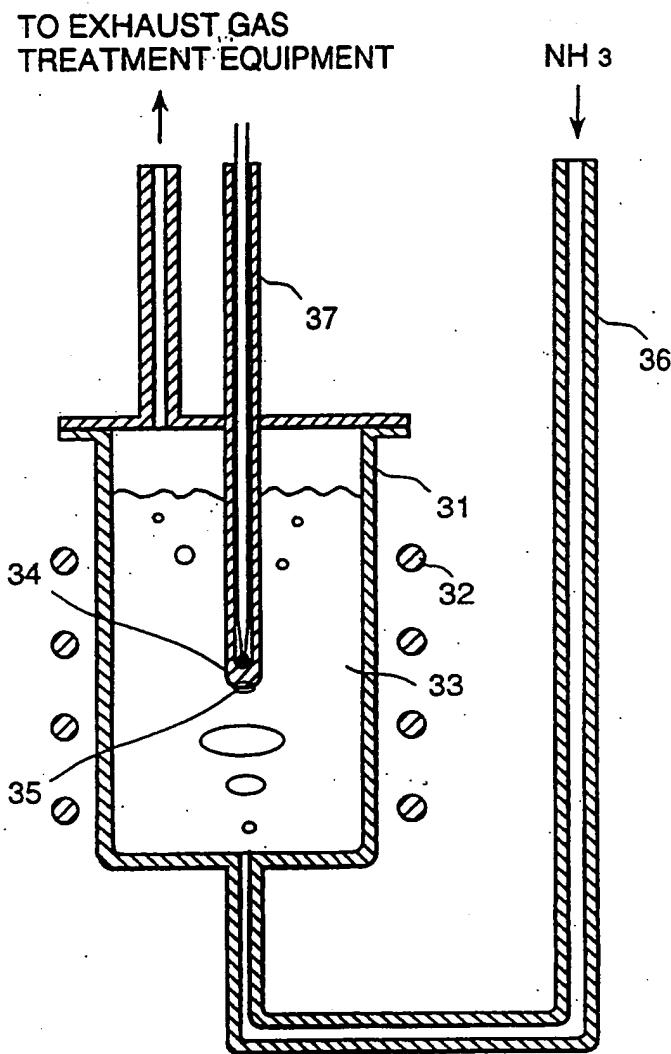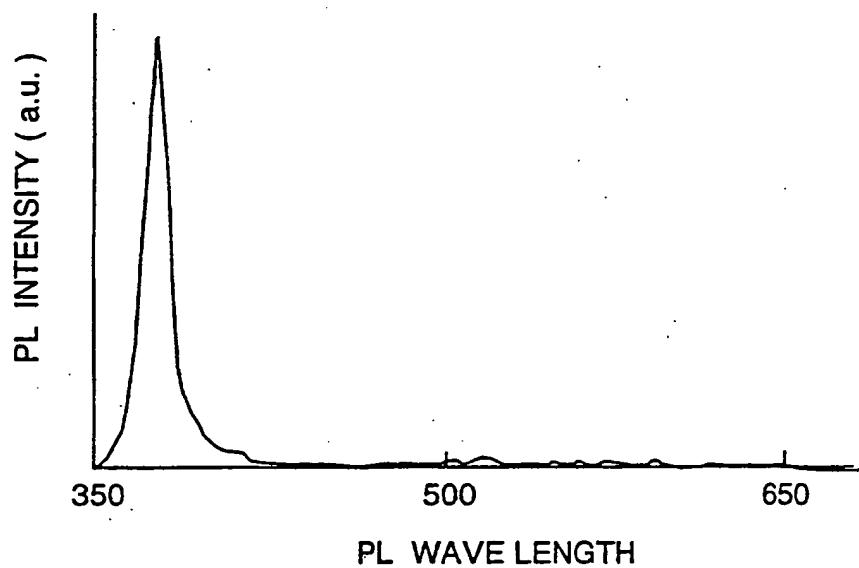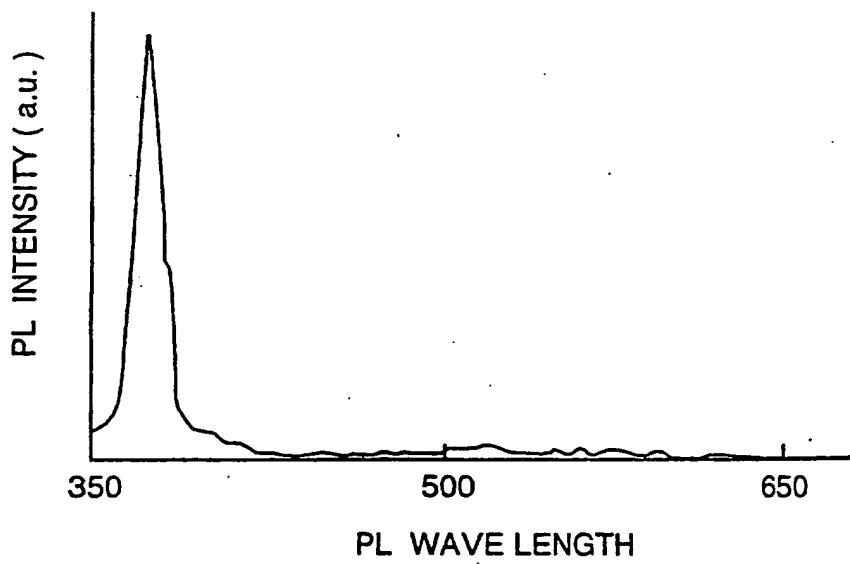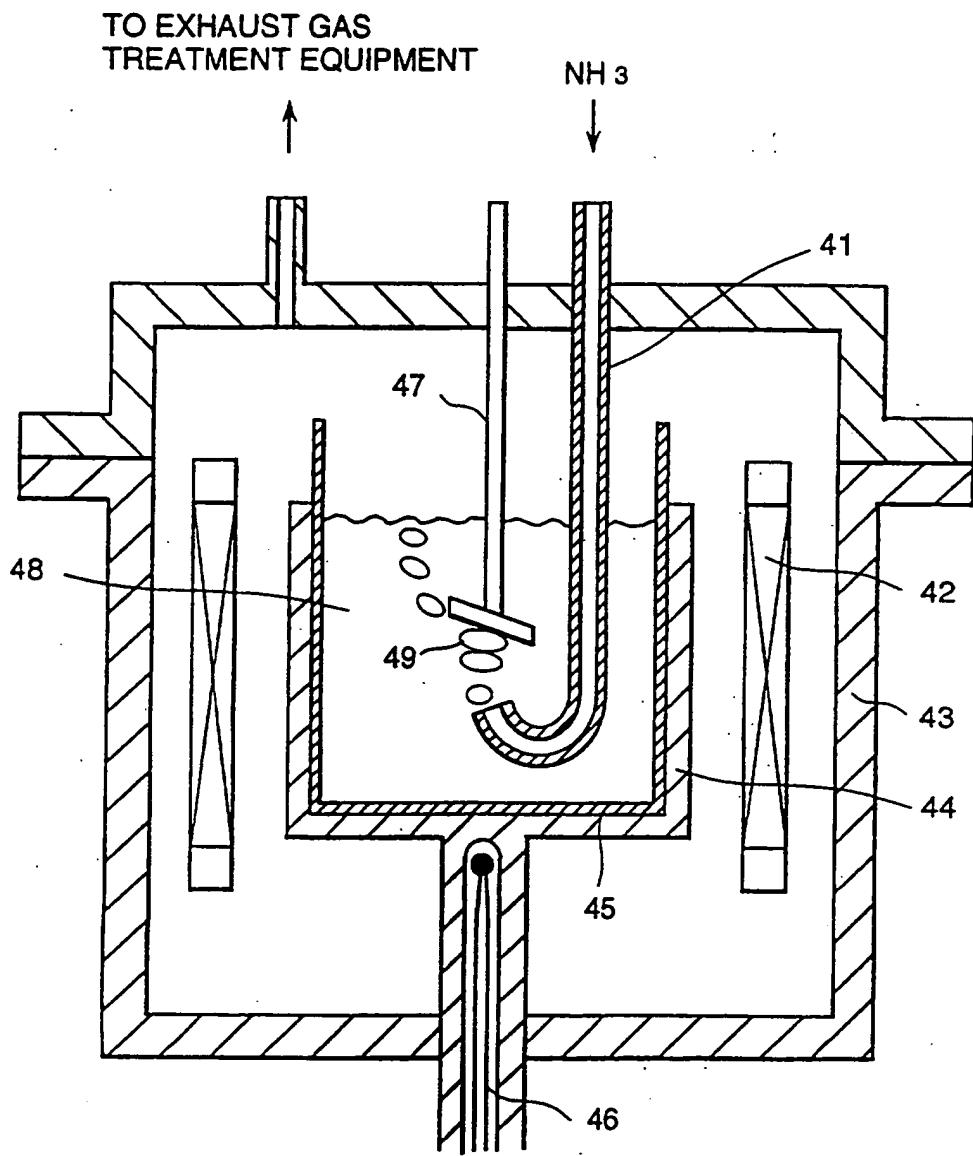
FIG. 13
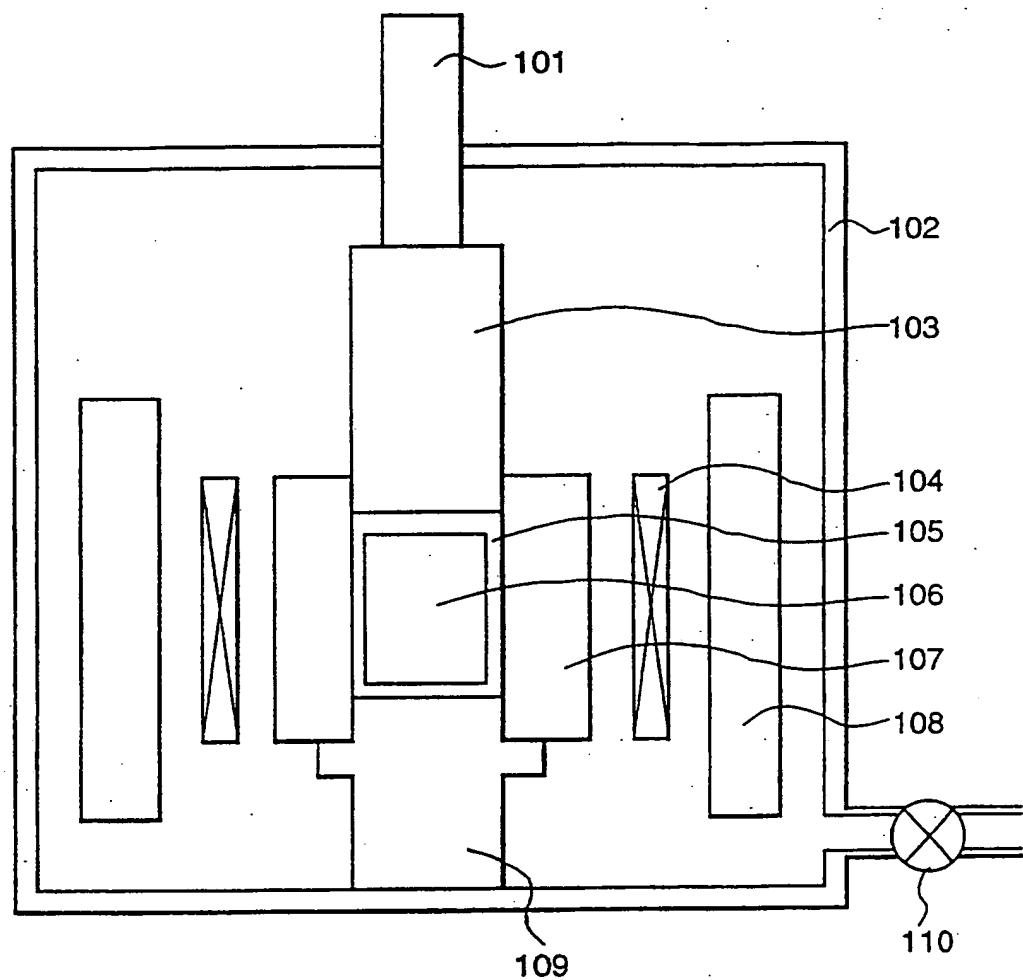
FIG. 14
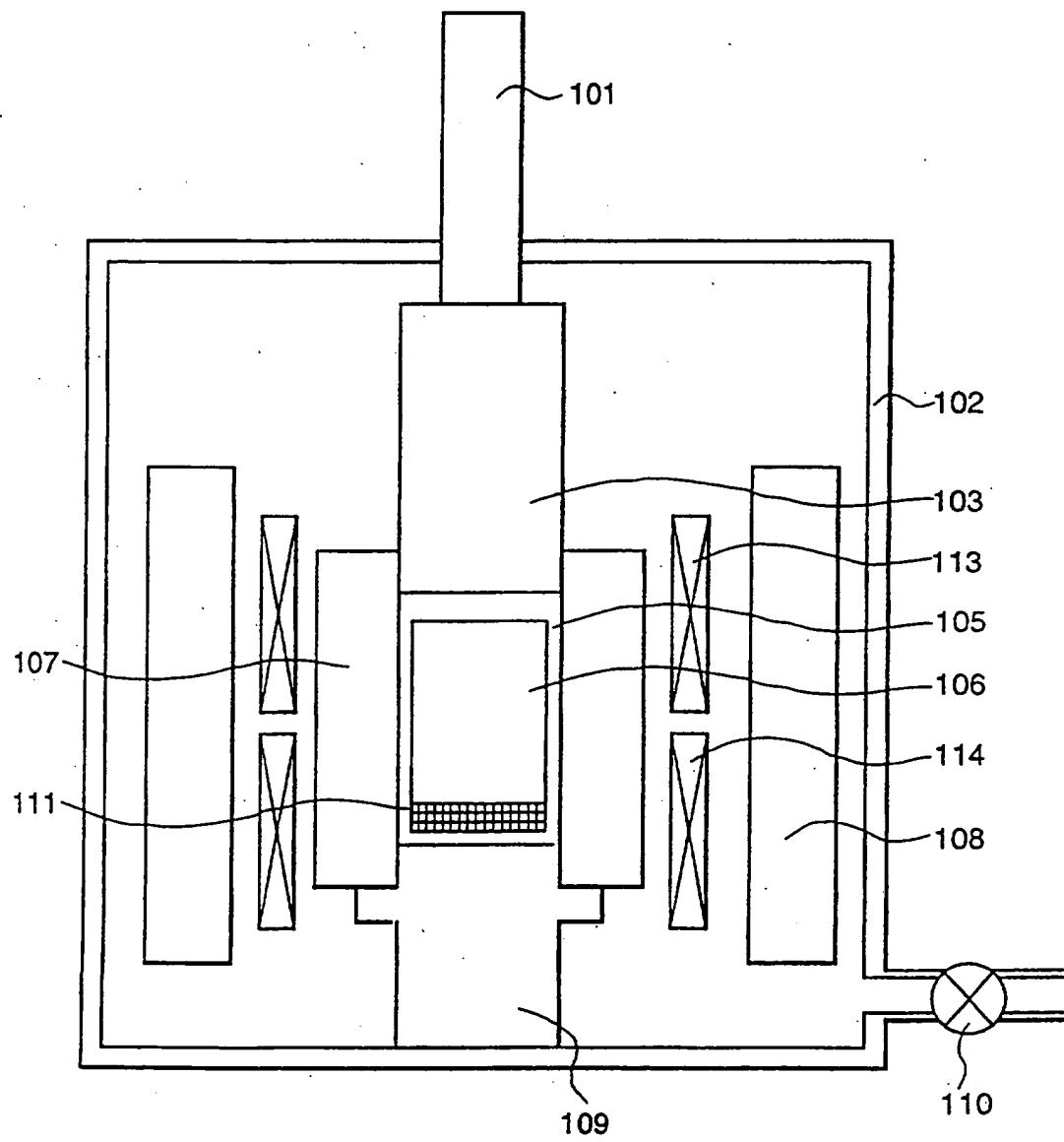
FIG. 15
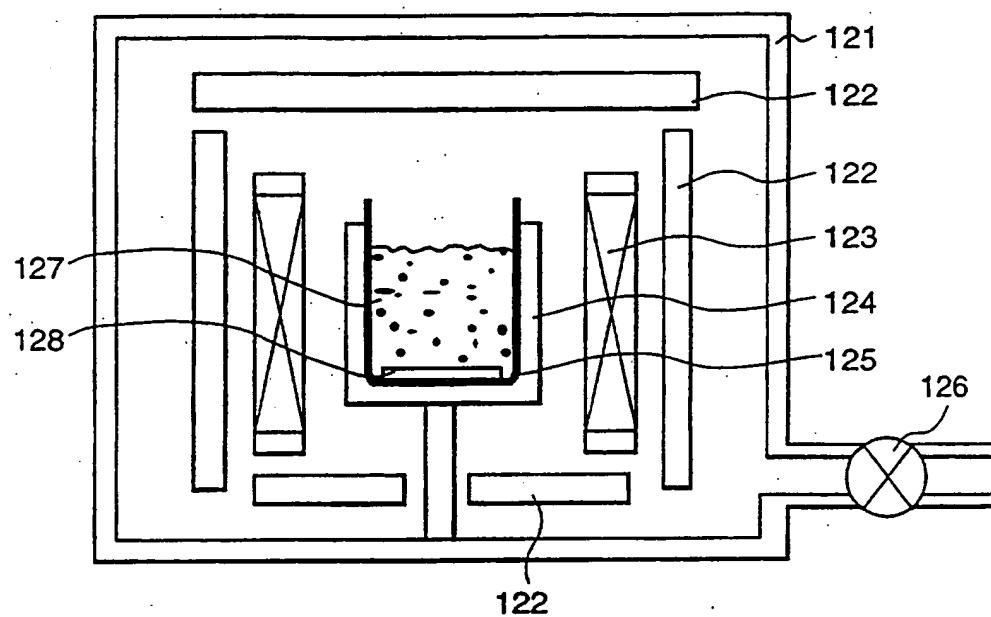
FIG. 16
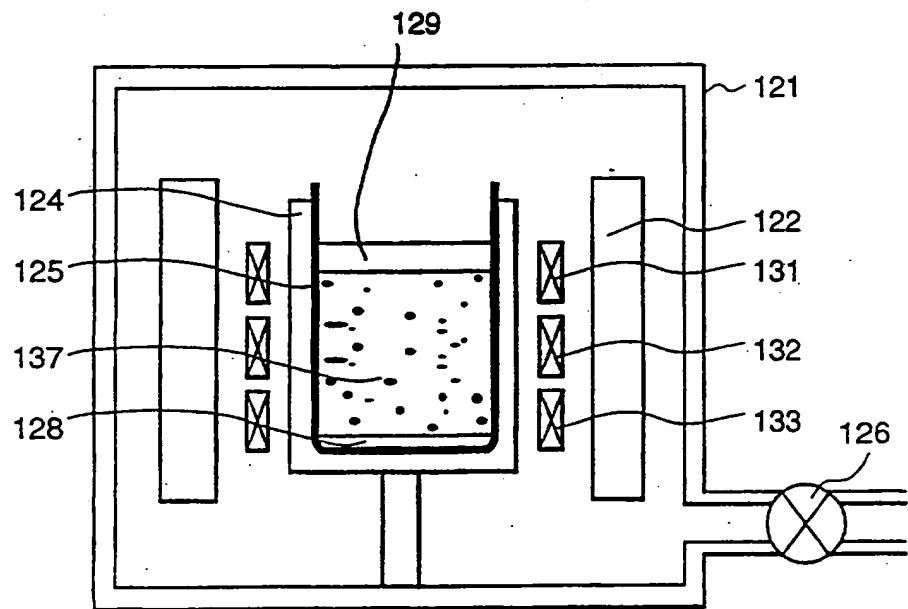
FIG. 17
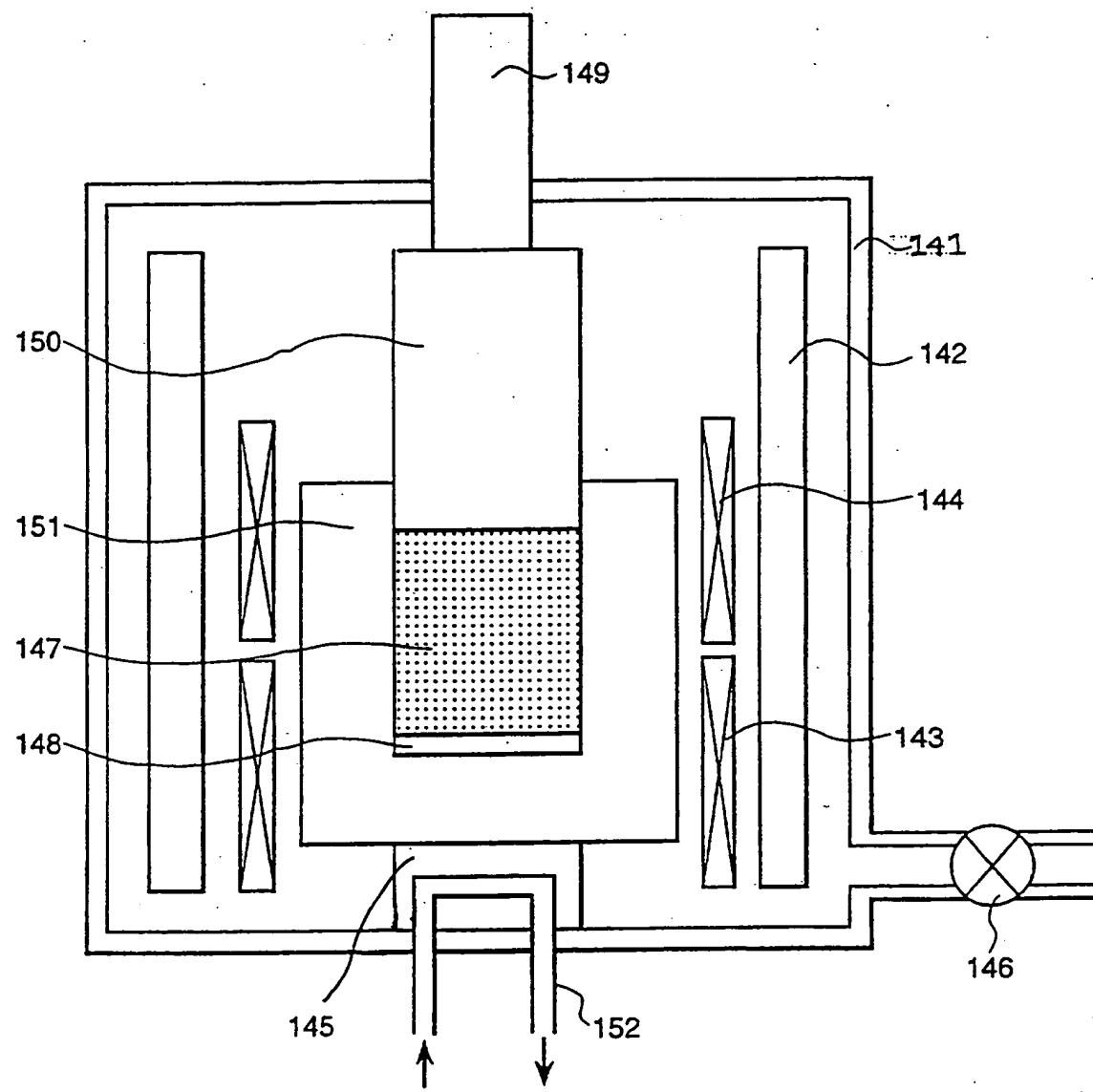
TITLE OF THE INVENTION

METHOD OF FABRICATING NITRIDE CRYSTAL,

LIQUID PHASE GROWTH METHOD, NITRIDE CRYSTAL, NITRIDE

CRYSTAL POWDERS, AND VAPOR PHASE GROWTH METHOD

BACKGROUND OF THE INVENTION

The present invention relates to a method of

fabricating a nitride crystal of a Group III element

such as a GaN, AlN, InN, or the like, a mixture, a

liquid phase growth method, a nitride crystal, nitride

crystal powders, and a vapor phase growth method.

A method of easily fabricating a Group III nitride

bulk crystal of GaN, AlN, InN or the like has never

existed. If a GaN bulk crystal can be made, its impact

is beyond imagination for realization of a blue laser

diode and the like. A bulk crystal of a wide band gap

semiconductor material will be fully used in the 21st

century.

As a method of fabricating GaN crystal powders, a

method of fabricating GaN crystal powders by the

reaction of a Ga oxide such as Ga_2O_3 to ammonia is put

into practical use. Powders fabricated by the method

are available on the market as a reagent.

A method of easily fabricating a Group III nitride

bulk crystal has not been developed. Although the

following literature by S. Porowski et al. is

published, since a very high pressure is necessary, it is dangerous and difficult to fabricate the crystal. However, the size of the obtained crystal is as small as about a few mm.

5   "Prospects for high-pressure crystal growth of III-V nitrides" by S. Porowski, J. Jun, P. Perlin, I. Grzegory, H. Teisseyre and T. Suski, Inst. Phys. Conf. Ser. No. 137: Chapter 4

      Paper presented at the 5th SiC and Related
10   Materials Conf., Washington, DC, 1993.

      A Group III nitride represented by GaN has a very high melting point and is decomposed and sublimated at a temperature lower than the melting point. Consequently, its melt cannot be produced and a
15   crystal cannot be grown from the melt. Since the solubility of the Group III nitride to a Group III solution is very low, it is also difficult to grow a crystal from the solution. Methods of growing a crystal of a Group III nitride which have been put
20   into practical use are only three kinds of vapor phase epitaxial growth methods of HVPE (Hydride Vapor Phase Epitaxial growth), MOVPE (Metal Organic Vapor Phase Epitaxial growth), and MBE (Molecular Beam Epitaxial growth). LEDs made of a GaN manufactured by using the
25   methods are available on the market. As an example of

the GaN crystal growth by MOVPE, the following

literature was published.

"Novel metal organic chemical vapor deposition

system for GaN growth", S. Nakamura, Y. Harada and M.

5   Seno, Appl. Phys. Lett. 58(18)6, 1991

In recent years, attention is paid to a nitride

crystal of a Group III element represented by GaN as a

material used for a blue light emitting device. In

order to produce the device, for example, it is

10   necessary to epitaxially grow a GaN crystal on a

substrate. In the epitaxial growth, it is ideal that

the lattice constant and the coefficient of thermal

expansion of the crystal as a substrate and those of a

crystal which is grown on the substrate are the same

15   in order to prevent occurrence of distortion in the

crystal to be grown. However, a bulk crystal of a

nitride which can be used as a substrate has not been

obtained. A sapphire substrate or the like having a

different lattice constant has to be used instead and

20   a crystal is epitaxially grown on the sapphire

substrate.

Although the MOVPE method is mainly used as an

epitaxial growth method at present, there are problems

such that an organic metal as a material catches fire

25   easily and is dangerous, and is expensive, and needs a

large-scaled complicated expensive growth system.
Hydrogen is inevitably contained as an impurity in the
grown crystal and it is consequently difficult to
increase the concentration of carriers of a p-type

5   crystal.

In order to increase the carrier concentration of
the p-type crystal, it is therefore necessary to
arrange a p-type dielectric layer on the surface of a
device and to perform a nitride crystal process. Since

10   it is necessary to arrange the p-type dielectric layer
on the surface of a device, the degree of freedom in
designing the device structure is low.

Another epitaxial growth method is an LPE (Liquid
Phase Epitaxial growth) method in which a Group III

15   nitride crystal is dissolved as a solute in a melt of
a Group III element and growing a liquid phase
epitaxial layer from the solution. A Group III nitride
crystal conventionally sold in the market is, however,
fine powders produced by reacting a Ga oxide such as

20   Ga_2O_3 in case of GaN with ammonia. The surface of the
GaN crystal is not easily wet due to the shape and
there is consequently a problem that the powders are
not easily dissolved in Ga.

Nitride crystal powders are expected to be applied

25   as a luminescent material and a dopant material in

liquid phase epitaxial growth of GaAs, GaP, and the like. The GaN crystal powders which are conventionally available on the market have a low purity for the cost and are unsuitable as a starting material for vapor phase growth. Since the powders are not easily dissolved in a semiconductor solution due to the shape, there is a problem that the powders are not easily used as a material for liquid phase growth or a dopant material.

On the other hand, a method called hot pressing in which a substance as a material is charged into a cylinder and heated and molded while pressurizing it by a piston is generally used for molding ceramics and the like.

According to the hot pressing, although a nitride such as AlN can be molded under pressure by using an appropriate binder, a single crystal growth has not been realized yet. This is because the melting point of a nitride crystal is very high and a nitride is decomposed before the temperature of the material reaches the melting point and nitrogen is escaped from the material.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a novel method of fabricating a nitride crystal, a

mixture, a vapor phase growth method, a nitride
crystal, nitride crystal powders, and a vapor phase
growth method which can solve the foregoing drawbacks
of the conventional techniques and easily and cheaply

5   obtain a nitride crystal of a Group III element having
a high   purity such as GaN.

It is another object of the invention to provide a
novel crystal growing method which can easily and
safely grow a bulk crystal of a nitride crystal of a

10   Group III element such as GaN which has not been
obtained and a novel crystal growing method which can
easily and safely epitaxially grow a Group III nitride
crystal.

The first point of the invention is, broadly, the

15   following three.

(1) A reaction is made by injecting a gas
containing nitrogen such as ammonia into a melt of a
Group III element such as Ga. Consequently, a large
amount of microcrystals of the Group III nitride are

20   floated to the surface of the melt of the Group III
element.

(2) A mixture of the Group III element and the
Group III nitride microcrystals which is obtained in
this manner is used as a material and a liquid phase

25   epitaxial growth of the Group III nitride crystal is

performed. The Group III element nitride microcrystal
obtained by the above method is easily wet by the
Group III element solution, so that the Group III
element microcrystals can be easily dissolved in the
5   Group III element melt.

(3) The Group III nitride microcrystal obtained
by removing the Group III element from the mixture by
acid cleaning or the like is used as a material to
grow the vapor phase of a Group III nitride crystal or
10 to produce a molten or sintered crystal. The material
obtained by this method has a high   purity and is
cheap.

Specifically, a method of injecting a vapor of a
Group V element into a Group III melt to synthesize a
15 Group III-V compound is called an injection method and
is a known technique. For example, as an example of
synthesizing a polycrystal of InP as one of Group III-
V compound semiconductors, there is an academic report
as shown below.

20 "Mass synthesis of InP polycrystal by the P-
injection method", Shibata et. al, the 34th Japanese
applied physics related association conference (1987)
28p-Z-1

The injection method is, however, so-called a melt
25 growth method in which the Group III melt is heated to

a temperature equal to or higher than the melting
point of the Group III-V compound as a synthesis, the
vapor of a Group V element is once injected to produce
a melt of the Group III-V compound, and the melt is

5   cooled to thereby produce a crystal. On the contrary,
a nitride synthesizing method according to claim 1 of
the invention is quite different from the conventional
injection method with respect to a point such that a
gas containing nitrogen is injected into a Group III

10   melt at a temperature much lower than the melting
point of the nitride to be obtained by the synthesis,
the liquid-phase Group III element and the vapor-phase
Group V element are reacted, and a solid-phase Group
III nitride microcrystal is directly formed in the

15   Group III element solution (it cannot be produced in
the melt of the nitride). The characteristic that the
solubility of a nitride to the Group III element melt
is very low is positively used.

In the nitride crystal fabricating method

20   according to claim 1, by mixing an impurity element
with the Group III metal element, a Group III nitride
crystal in which an impurity is doped can be
fabricated (claim 2). By using the nitride crystal
fabricating method according to claim 1 or 2, a

25   mixture of the Group III nitride powders and the Group

III metal material can be obtained (claim 3).

A mixture of the Group III nitride crystal and the Group III metal material according to claim 4 of the invention is especially characterized in that,

5   although the Group III nitride crystal is a microcrystal, the surface is completely wet by the Group III metal element. When crystal fine powders are added to a material for liquid phase growth or a dopant, the fine powder having a surface area which is

10   large for the volume is not easily wet by the Group III melt, so that there is a problem that the fine powders are not easily dissolved. Especially, in a nitride crystal having a low saturation solubility, the low solubility is a critical drawback for crystal

15   growth. The Group III nitrides which are conventionally available on the market are in almost fine powder states and unconditionally have the foregoing drawback.

In the conventional Group III nitride synthesizing

20   method, since a Group III oxide or chloride is used as a material, a process for removing a nonreacted material from the synthesized nitride powders is always necessary. Since an oxide or chloride is not used as a material in the fabricating methods

25   according to claims 1, 2, and 4 of the invention, an

unreacted material does not become an impurity at the
time of liquid phase growth. When the oxide or
chloride is not used as a material for liquid phase
growth, the mixture can be therefore directly used as

5   a material for liquid phase growth without extracting
only the group III nitride. If the extracting process
can be omitted, not only the process can be largely
shortened but also contamination of the material which
tends to occur in the extracting process can be

10   prevented, so that the liquid phase growth with high
impurity can be realized.

Although the invention according to claims 3 and 4
relates to a liquid phase growth method, the invention
can be also applied to a vapor phase growth method.

15   That is, the invention according to claim 5 relates to
Group III nitride crystal powders obtained by removing
the Group III metal material from the mixture and the
Group III metal material obtained by the nitride
crystal fabricating method according to claim 1 or 2.

20   The invention according to claim 7 relates to a
method of fabricating a Group III nitride crystal
which is obtained by melting and re-solidifying or
sintering the Group III nitride powders according to
claim 5 and re-solidifying or sintering the melt.

25   The second point of the invention is a method of

immersing a seed crystal or a substrate crystal into a
melt of a Group III element such as gallium, allowing
bubbles of a gas containing nitrogen such as ammonia
to intermittently come into contact with the surface

5   of the crystal, and reacting the Group III element
with the gas containing nitrogen on the surface of the
seed crystal or the substrate crystal, thereby growing
a Group III element nitride crystal on the surface of
the crystal.

10   The nitride crystal growing method is also on the
condition that the gas containing nitrogen is injected
into the melt of a Group III element at a temperature
much lower than the melting point of the nitride to be
synthesized and the liquid-phase Group III element is

15   reacted with the vapor-phase Group V element, thereby
directly forming the solid-phase Group III nitride
crystal in the Group III element melt (a melt of
nitride cannot be produced in the melt of a nitride).
The characteristic such that the solubility of a

20   nitride to a Group III element melt is very low is
positively used. The condition itself is a crystal
growing method based on a novel concept which is quite
different from the growing method using a melt such as
the above-mentioned injection method.

25   It is known that a Group III element such as

gallium, aluminium, indium, or the like and a gas
containing nitrogen such as ammonia, hydrazine, or the
like react with each other at a temperature about few
hundreds to 1000°C which is considerably lower than the
5   melting point of a nitride (it is said 2000°C or higher
in case of GaN) and a Group III nitride is formed. For
example, there is a report as shown below.

"Crystal growth of GaN by reaction between Ga and
NH$_3$," D. Elwell et. al., J. Crystal Growth 66 (1984) 45
10   - 54

However, the GaN formed is not dissolved in the
Group III melt but is covered over the surface of the
Group III melt.

In a nitride crystal fabricating method according
15   to claim 8 or 9, a seed crystal or a substrate crystal
is immersed in a melt of a Group III element such as
gallium and bubbles of a gas containing nitrogen such
as ammonia are intermittently come into contact with
the surface of the crystal. By the reaction between
20   the Group III element and the gas containing nitrogen
on the surface of the seed crystal or the substrate
crystal, the Group III atoms connected to the surface
of the seed crystal or the substrate crystal are
nitrided and a nitride crystal can be epitaxially
25   grown on the substrate. By continuously repeating the

reaction, an epitaxial film or a bulk crystal can be grown.

In the nitride crystal fabricating method according to claim 8 or 9, the Group III element is either Al, Ga, or In and ammonia gas can be also used as the gas containing the nitrogen atoms (claim 10).

A nitride crystal growing method as a third point of the invention is characterized by including a process for charging nitride crystal powders and a liquid encapsulating material into a cylinder and for heating the materials while pressurizing by a piston.

After producing a melt of a nitride by heating under pressure, the nitride melt can be solidified in a process for returning the pressure and the temperature to normal pressure and temperature. It is also possible to heat the nitride crystal powders until just before a melting point of the nitride and to occur a solid-phase growth of the nitride crystal. The nitride crystal powders may be preliminarily molded under pressure. It is preferable that the starting material of a nitride is GaN crystal powders synthesized by the injection method. Preferably, the material powders are exposed in vacuum or in a nitrogen atmosphere at least until the liquid encapsulating material melts. It is preferable that

the nitride material in the cylinder has a temperature gradient. It is preferable to arrange the seed crystal on the low temperature side in the nitride material. It is preferable to repeat temperature increase and

5   decrease and/or pressure increase and decrease during the crystal growth. A component element of the nitride crystal can be used as a binder when the nitride crystal powders are molded under pressure.

A method of growing a Group III nitride crystal

10   according to the invention for heating a flux and Group III nitride crystal powders under pressure to dissolve the Group III nitride crystal powders in the flux, and after that, cooling the solution, thereby growing a Group III nitride crystal, is characterized

15   in that the heating temperature of the flux is 800°C or higher and the flux contains at least one of Ga, In, Pb, Sn, Bi, and Na.

Preferably, the flux and the Group III nitride crystal powders as materials are a mixture of the

20   Group III element and the Group III nitride crystal powders obtained by the injection method. The flux in which the Group III nitride as a material is dissolved has a temperature gradient. By cooling the solution, the Group III nitride crystal can be deposited on the

25   low temperature side. The seed crystal is arranged in

the flux and the Group III nitride crystal can be deposited on the seed crystal. It is preferable to float a liquid encapsulating agent on the flux. A cylinder and a piston can be used as pressurizing

5   means.

A method of growing a Group III nitride crystal according to another embodiment of the invention will be described.

(1) The point of the embodiment is that, when a

10   nitride as a material is heated and pressurized, a liquid encapsulating material is used in order to prevent decomposition or sublimation of the nitride.

As a modification of the hot pressing, HIP (hot isotropic pressing) is known. HIP is a method of

15   performing hot pressing by using an appropriate medium in order to uniformly apply pressure to a sample. Another powders which do not react with the gas or the sample are generally used as a medium in HIP since the property of release from the sample is regarded as

20   important. The medium is not effective on suppressing the decomposition or sublimation of the material. This is the point different from the present invention using the liquid encapsulating agent. On the other hand, since the liquid encapsulating agent in the

25   embodiment also acts as a medium, the nitride material

can be isotropically pressurized and uniform crystals can be consequently grown.

As a starting material of the nitride, the GaN crystal powders fabricated by the injection method of the invention can be also used. The powders fabricated by the method have a high purity and a fine grain size and are regular in size. Consequently, pressure can be easily applied isotropically in pressurizing operation, so that a uniform crystal having a high purity can be grown. Since a large amount of GaN powders can be easily obtained at low cost in the injection method, it is also effective to reduce the manufacturing cost of the GaN single crystal.

As a binder, a construction element of the nitride crystal can be used. For example, in case of the GaN crystal growth, it is preferable to add and mix a small amount of a metal Ga to GaN powders and to grow a crystal by using the mixture as a starting material. It is means for holding the purity of the grown crystal. From the point of view, it is desirable not to use a substance containing a component which becomes an impurity as a binder.

It is preferable to expose the material powders in vacuum until the liquid encapsulating material melts in order to remove a gas existing in the powder

particles of the material so that bubbles are not formed in the grown crystal and the liquid encapsulating agent. It is also preferable to put the material powders in nitrogen in order to put a nitrogen gas into the powders of the material. The nitrogen gas is dissolved in the material solution so that a nitride is synthesized as much as possible.

It is preferable that the material has a temperature gradient so that the crystal growing direction is limited to one direction from the low temperate side to the high temperature side to grow a bulk uniform single crystal. A case of arranging the seed crystal on the low temperature side has a similar purpose.

It is preferable to set the height of the material larger than the diameter, so that the temperature gradient of the material during the crystal growth becomes larger in the longitudinal direction than in the radial direction. Consequently, the crystal is easily grown in the above-mentioned one direction.

The pressure and the temperature can be repeatedly increased and decreased, so that the nucleus of the nitride crystal is deposited and re-dissolved, and a superior growth nucleus is selectively left, thereby growing a bulk nitride single crystal grain.

(2) The point of another embodiment of the
invention is that powders of Group III nitride crystal
itself are used as a material as a solute in a method
using a flux and the surface of each of the material
5 powders is preliminarily covered by the flux so that
the powders are not sublimated or decomposed.

The method of using the powders of the crystal to
be grown as a material of the flux method seems
obvious and is a flux method generally used for an
10 oxide crystal growth. In the Group III nitride crystal
growth, however, the flux method in which Group III
nitride crystal itself is used as a material has never
been reported. As the reasons, it can be mentioned
that, first, the fabrication itself of the Group III
15 nitride crystal powders is difficult and it is
difficult to acquire the material and, second, the
powder material has a low density and is easily
floated on the flux, the surface of the material is
not easily wet by the flux and consequently is not
20 easily dissolved in the flux. Although it can be
considered that the powders are dissolved easier if
the grain size of the material powder is enlarged, a
method of easily acquiring the Group III nitride
crystal having a large grain size has not been
25 reported under the present conditions.

However, by the method of claim 1 or claim 2 of the subject invention, the Group III nitride crystal powders can be easily produced, so that the first problem is solved. Further, the mixture of a Group III nitride microcrystal and a Group III metal material according to claim 3 is used, the second problem can be also solved.

Further, as a result of examinations, it was found out that even when GaN powders fabricated by a method except for the injection method, for example, a method of reacting gallium chloride with ammonia gas at a high temperature are used, if the GaN powders are mixed well with Ga which is preliminarily melt and the surface of each of the GaN powders is covered by the flux, sublimation and decomposition can be suppressed to a degree which is ignorable. The effect was also recognized not only in the case of using Ga as a flux but also in the case where a flux including at least one of In, Pb, Sn, Bi, and Na is used.

The reason why GaN is grown at a temperature equal to or higher than 800°C in the embodiment is because the mode of the crystal growth of GaN is changed after 800°C.

That is, the higher the temperature of the flux is, the more GaN is dissolved in the flux. Consequently,

in order to efficiently grow the crystal, the growth
temperature is preferable to be higher. Since the
solubility of GaN to the flux is continuously changed
with temperature, it does not mean that the solution
5   quantity is changed after 800°C. However, it was found
out that when the GaN crystal is grown at a
temperature lower than 800°C, the dissolved GaN is
again deposited only on the surface of each of the
undissolved GaN powders and a bulk crystal cannot be
10 grown even if the pressure and the cooling time are
changed.

On the other hand, it was found out that, at a
temperature equal to or higher than 800°C, although a
deposition is seen on a undissolved powder, a new
15 crystal nuclei is grown in a low temperature part of
the flux. As a result, it leads the method of growing
a bulk GaN single crystal.

Although it is difficult to grow a bulk crystal in
a low temperature around 800°C, if the flux has a
20 temperature gradient and a crystal is grown by a
method using a temperature difference, it is not
impossible.

It is necessary to perform a work of wetting the
surface of the GaN powder as a material by the flux at
25 a temperature lower than 800°C since the sublimation or

decomposition of GaN starts when the temperature
exceeds 800°C. The melting point of a material used as
a flux has to be therefore lower than 800°C.

As a material used as a flux, in addition to the
5   condition that the melting point is lower than 800°C,
it is necessary to choose a material into which GaN
can be dissolved and which does not form another
compound by the reaction with GaN. For example, in
case of growing a GaN crystal, aluminium or the like
10   satisfies the former condition but forms AlN by the
reaction with GaN, so that it cannot be used as a flux.
As a flux for growing a GaN crystal, it has to be
stable without being decomposed at a temperature high
enough to dissolve GaN.

15   As a flux, a material obtained by mixing Bi with
Ga can be used. The material has an advantage that the
occurrence frequency of deposited nuclei is suppressed
at the time of the GaN crystal growth and the yield of
the single crystal is improved.

20   In order to suppress elimination of GaN from the
flux and evaporation of the flux itself, it is
preferable to pressurize after the surface of the flux
is covered by a liquid encapsulating agent. As the
pressurization gas in this case, any kind of gas can
25   be used as long as it has a property that it does not

cause any inconvenience by the reaction with the liquid encapsulating agent or a component material of the apparatus. It is obviously understood that the material can be mechanically pressurized by a piston

5   or the like.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic cross section of a GaN crystal synthesizing system according to first to

10   seventh embodiments of the invention;

Fig. 2 is a schematic cross section of a liquid phase growth system of a GaN crystal according to a second embodiment of the invention;

Fig. 3 is a graph showing a temperature program

15   when a liquid phase of the GaN crystal according to the second embodiment of the invention is grown;

Fig. 4 is a diagram showing a photoluminescence measurement result at a room temperature of a liquid phase epitaxial growth undope GaN crystal film

20   according to a second embodiment of the invention;

Fig. 5 is a diagram showing a photoluminescence measurement result at a room temperature of a liquid phase epitaxial growth Si doped GaN crystal film according to a third embodiment of the invention;

25   Fig. 6 is a diagram showing a photoluminescence

measurement result at a room temperature of a liquid

phase epitaxial growth Mg doped GaN crystal film

according to a fourth embodiment of the invention;

Fig. 7 is a diagram showing a photoluminescence

5   measurement result at a room temperature of undoped

GaN microcrystal powders according to a fifth

embodiment of the invention;

Fig. 8 is a schematic cross section of a vapor

phase growth system of a GaN crystal according to a

10   sixth embodiment of the invention;

Fig. 9 is a schematic cross section of a GaN

crystal growth system according to an eighth

embodiment of the invention;

Fig. 10 is a diagram showing a photoluminescence

15   measurement result at a room temperature of the GaN

crystal fabricated in the eighth embodiment of the

invention;

Fig. 11 is a schematic cross section of a GaN

crystal epitaxial growth system according to a ninth

20   embodiment of the invention;

Fig. 12 is a diagram showing a photoluminescence

measurement result at a room temperature of a GaN

epitaxial growth crystal fabricated in the ninth

embodiment of the invention;

25   Fig. 13 is a cross section showing a crystal

growth system used for another embodiment of the

invention;

Fig. 14 is a cross section showing a crystal

growth system used for another embodiment of the

5   invention;

Fig. 15 is a cross section showing a GaN crystal

growth system used for further another embodiment of

the invention;

Fig. 16 is a cross section showing a GaN crystal

10   growth system used for further another embodiment of

the invention; and

Fig. 17 is a cross section showing a GaN crystal

growth system used for further another embodiment of

the invention.

15

Detailed Description of the Preferred Embodiments

Embodiments of the invention will be described

hereinbelow.

(Embodiment 1)

20   As an embodiment of the invention, an apparatus

shown in Fig. 1 was produced. An example of

synthesizing a GaN microcrystal by using the apparatus

will be described.

3000g of Ga was charged in a quartz crucible 1

25   having the inner diameter of 70 mm and the height of

150 mm and Ga was heated to 950°C by a heater 2, thereby obtaining a Ga melt 3. Ammonia gas was injected into the Ga melt 3 via a gas introduction pipe 4 at a flow of 0.5l/min for five hours. The

5   injected gas into the melt 3 reacted with the melt to thereby form GaN microcrystals. The GaN microcrystal was floated to the surface of the Ga melt. Ammonia gas which did not contribute to the reaction became bubbles, passed through the melt 3, escaped to the

10   space in the upper part of the vessel, and were exhausted to the outside of the vessel via an exhaust pipe 5. The exhausted ammonia gas was discharged to the atmosphere via wet type exhaust gas treatment equipment. After the gas injection for five hours, the

15   gas injected was changed to nitrogen and the Ga melt was cooled to a room temperature.

The cooled Ga melt was taken out from the vessel and observed. A large amount of GaN microcrystals were floated on the Ga melt. The surface of the GaN

20   microcrystal was completely wet by the Ga melt. Increase in the weight of the Ga melt of 10.2g was recognized after the synthesis work as compared with the Ga melt before the work. According to calculation based on the weight increase, 61g of GaN microcrystals

25   was synthesized.

(Embodiment 2)

The GaN microcrystal was synthesized in a manner similar to the first embodiment, a mixture of the Ga melt and the Ga microcrystal floated on the Ga melt was used as a material, and liquid phase epitaxial growth of GaN was performed by a slide boat method. Fig. 2 is a schematic cross section of an apparatus used for the growth. Fig. 3 shows a temperature program at the time of the liquid phase epitaxial growth. 20g of the mixture of the Ga melt and the GaN microcrystal as a material 12 was put in a graphite boat 11. On a slide boat 17, a c-face sapphire substrate 16 of (25 × 25 mm) was set. A quartz reaction tube 14 had therein a nitrogen gas flow atmosphere and the material was heated by heaters 13 until an output of a thermocouple 15 became 1150°C. After the material was left for four hours in such a state, the temperature was lowered to 1100°C, the slide boat 17 was moved by pulling an operation rod 18 and the sapphire substrate 16 came in contact with the material 12. After that, the temperature of the material was lowered to 600°C at a rate of 1°C per minute, the operation rod 18 was pushed to return the slide boat 17 to the original position, and the

substrate 16 and the material 12 were separated. The
power source of the heater was turned off and the
material 12 was cooled to the room temperature.

The substrate to which the growth was performed
5   was taken out and the surface and the cross section
were observed. A transparent film was grown on the
sapphire substrate. The film thickness obtained by the
SEM observation of the cross section was 4.2 μm. A
photoluminescence measurement result of the grown film
10   at a room temperature is shown in Fig. 4. A sharp
light emission peak of 360 nm corresponding to a band
edge emission of GaN shown in Fig. 4 was observed and
the grown film was confirmed to be a high-quality GaN
film. The electric characteristics of the grown film
15   were measured by the Van der Pauw method. Preferable
characteristics such as the carrier concentration of 1
× 10^{17} cm^{-3} and mobility of 520 cm^2/V·sec were shown.

(Embodiment 3)
20   In a manner similar to the first embodiment, 20 mg
of Si was preliminarily added to the material Ga and
the GaN microcrystal was synthesized, a mixture of the
obtained Ga solution and GaN microcrystal was used as
a material, and liquid phase epitaxial growth of GaN
25   was performed by a slide boat method similar to that

of the second embodiment.

Fig. 5 shows a result of photoluminescence measurement of the obtained GaN film at a room temperature. A sharp light emission peak of 369 nm corresponding to light emission of Si doped GaN was observed and it was confirmed that Si was doped on the grown film. The carrier concentration of the grown film was measured by the Van der Pauw method and was found to be 6×10^{18} cm^{-3} of the n-type.

(Embodiment 4)

In a manner similar to the first embodiment, 7 mg of Mg was preliminarily added to the material Ga and the GaN microcrystal was synthesized, a mixture of the obtained Ga solution and GaN microcrystal was used as a material, and liquid phase epitaxial growth of GaN was performed by a slide boat method similar to that of the second embodiment.

Fig. 6 shows a result of photoluminescence measurement of the obtained GaN film at a room temperature. A light emission peak of 445 nm corresponding to light emission of Mg doped GaN was observed and it was confirmed that Mg was doped in the grown film. The carrier concentration of the grown film was measured by the Van der Pauw method and was 5

$\times 10^{17}$ cm^{-3} of the p-type. According to the Mg doped
GaN film obtained in the method, although Mg in the
crystal is not activated if heat treatment is not
performed to the film obtained by the MOVPE growth and

5   p-type electric characteristics are not shown,
preferable p-type electric characteristics are shown
in an as-grown state. It can be considered that the
hydrogen atoms which prevent the activation of Mg were
not doped.

10

       (Embodiment 5)
       A mixture of an undoped GaN microcrystal
synthesized by a method similar to that of the first
embodiment and a metal Ga was extracted, hydrochloric

15   acid and hydrogen peroxide water were added to the
mixture, and only Ga was dissolved, after that, only a
GaN microcrystal was filtered by a filter paper. The
filtered powders were sufficiently cleaned by pure
water and were dried in a vacuum high temperature

20   vessel. Consequently, 61g of white gray powders were
obtained. When the powders were observed by a
microscope, the powders were constructed by
microcrystals each in basically a hexagonal column
shape having a grain size of about 10 μm. The result

25   of photoluminescence measurement at a room temperature

of the powder is shown in Fig. 7. A sharp light

emission peak of 360 nm corresponding to GaN band edge

emission was observed and it was confirmed that the

obtained microcrystal is high-quality GaN. The

5   concentration of impurities which can be contaminated

in the obtained powders was checked by the secondary

ion mass spectroscopy (SIMS). Although about 5×10^{15}

cm^{-3} of Si which seems to be doped from the quartz

container was detected, others were below the

10   detection limits.

(Embodiment 6)

The GaN microcrystal powders obtained in the fifth

embodiment were used as a material and vapor epitaxial

15   growth of GaN was performed by an apparatus as shown

in Fig. 8. 25g of GaN microcrystal powders 26 as a

material were charged into a quartz crucible 23 having

the diameter of 50 mm. The quartz crucible 23 was

supported by a graphite susceptor 25 and was set in a

20   quartz vessel 21. On the other hand, a c-face sapphire

substrate 28 of (25 mm x 25 mm) was fixed by a

substrate holder 22 made of graphite and was suspended

in the quartz crucible 23 so that the surface of the

substrate faces the material 26. In such a state, the

25   inside of the quartz vessel 21 was substituted by an

ammonia gas atmosphere. While flowing the ammonia gas by 0.5 l/min, the material was heated by heater 24. The heating was controlled by an output of a thermocouple 27 arranged below the crucible so as to

5   be 1100°C. In this instance, the surface temperature of the substrate 28 was about 850°C. The crystal was grown by sublimation by holding the material in a heated state for 24 hours.

A transparent GaN film was grown on the surface of

10   the sapphire substrate which was taken out. When the surface of the GaN film was observed by a microscope, triangle to hexagonal morphologies were observed. The average thickness of the grown film was about 400 μm. When the electric characteristics of the grown film

15   were measured by the Van der Pauw method, preferable characteristics of the carrier concentration of 2 × 10^{17} cm^{-3} and the mobility of 490 cm^2/V · sec were shown.

(Embodiment 7)

20   In a manner similar to the first embodiment, InN was synthesized by using In instead of Ga. The same conditions as those of the first embodiment except for the synthesis temperature of 600°C were used. Synthesized In was cooled to 180°C and the mixture of

25   InN microcrystals and the metal In floated on the In

solution were taken out before In solidifies.

After hydrochloric acid and hydrogen peroxide
water were added and only In was dissolved, the
solution was filtered by a filter paper and only the

5   InN microcrystals were taken out. The powders obtained
by the filtering were sufficiently cleaned by pure
water and dried in a vacuum high temperature vessel.
As a result, about 200g of light white gray powders
were obtained. When the powders were observed by a

10 microscope, the powders were constructed by
microcrystals each basically in a hexagonal column
shape having a grain size of about 8 μm. When the
photo luminespectral of the obtained powders was
measured, light emission of 650 nm corresponding to a

15 band edge emission of InN was observed.

(Modification)

Although the GaN crystal growth has been mainly
described and also the InN crystal growth has been

20 mentioned in the foregoing embodiments, the invention
can be also applied to crystal growth of AlN, and
AlGaN, GaInN, and the like as mixed crystals of AlN or
InN.

As a gas containing nitrogen, except for ammonia,

25 it can be considered to use hydrazine, mono methyl

hydrazine, or the like.

Although the embodiment of the liquid-phase crystal growth under atmosphere has been described, when the crystal is grown under a high-pressure

5   atmosphere of nitrogen or ammonia, the crystal growth speed can be further increased.

Although the embodiments of the liquid-phase growth and the vapor-phase growth have been described with respect to the epitaxial growth on the sapphire

10   substrate, the invention can be also applied to epitaxial growth using another substrate or a nitride bulk crystal growth.

The yield and the grain size of the nitride microcrystal obtained by the synthesis can be

15   controlled by residence time of the gas such as ammonia injected into the Group III melt. Modifications such that the shape of the end of a gas injection tube is changed and a path through which bubbles of gas escape is formed by quartz work or the

20   like in the solution can be therefore considered.

(Other embodiments)

The nitride microcrystal obtained by the invention can be widely applied as a semiconductor material or

25   luminescence material. Especially, the liquid phase

growth method according to the invention is effective
when applied to fabrication of ultraviolet - yellow
light emission devices.

For example, when material housing parts are
provided in two positions in the liquid phase growth
apparatus described in the second embodiment and an Mg
doped GaN material is charged in one of the parts and
an Si doped GaN material is charged in the other part,
the GaN films of the p-type and the n-type can be
continuously grown on a substrate. When an LED
fabricating process is performed to the epitaxial
growth substrate obtained in this manner, a blue LED
of a p-n junction type can be easily fabricated.
According to the method, an LED can be manufactured
easily and safely at low cost as compared with the
conventional MOVPE. For GaN grown by the conventional
MOVPE, it is necessary to additionally perform heat
treatment in order to form a p-type crystal.
Consequently, there is limitation that the structure
of an element has to be designed so that the surface
of the crystal is always of the p-type. By using the
liquid phase epitaxial growth method according to the
invention, since the p-type conductivity can be
obtained without performing heat treatment, tolerance
in designing of the element structure can be largely

increased.

Since the nitride synthesis temperature, the atmosphere pressure, the dose of the material, and the like differ according to the kind of the nitride to be synthesized and the kind of a material to be used, it is difficult to unconditionally determine the optimum conditions.

(Embodiment 8)

As an eighth embodiment of the invention, an apparatus as shown in Fig. 9 was manufactured. An example in which the GaN crystal was grown by using the apparatus will be described.

3000g of a molten Ga 33 was charged into a quartz vessel 31 having the inner diameter of 70 mm and the height of 200 mm and a piece of an SiC single crystal of (6 mm × 6 mm) was attached as a seed crystal 35 to the end of a seed crystal supporting jig 34 and was fixed in the molten Ga 33. In such a state, the molten Ga 33 was heated by heaters 32 and was controlled to 1000°C by an output of a thermocouple 37.

Subsequently, ammonia gas was introduced from the bottom of the quartz vessel 31 via an ammonia introduction tube 36 made of quartz having the inner diameter of 6 mm at a ratio of 0.2 1/min for 76 hours.

The ammonia gas introduced in the molten Ga 33 rose as bubbles in the melt. The number of bubbles per minute was about 350. The bubbles of the ammonia gas rising in the melt collide with the surface of the seed crystal 35 and GaN crystals were sequentially formed on the seed crystal. The unreacted ammonia gas reached as bubbles the surface of the molten Ga and was exhausted to the outside of the vessel. The exhausted gas was treated by a wet scrubber and was released to the atmosphere. The bubbles of the ammonia gas reacted with Ga in places other than the surface of the seed crystal, thereby forming GaN microcrystals having the diameter of about few μm which were floated to the surface of the molten Ga and did not contribute to the growth on the seed crystal.

The grown crystals were cooled and taken out from the molten Ga. The metal Ga adhered on the surface was cleaned by hydrochloric acid. As a result, a GaN crystal of a hexagonal column shape having the diameter of about 10 mm and the height of about 6 mm was derived. The obtained crystal is transparent yellowish brown. It was confirmed by X-ray diffractometry that the obtained crystal was the GaN crystal. The full width at half maximum (FWHM) of an X-ray diffraction peak is about 2 min. It can be said

that the obtained crystal has a preferable crystallinity.

Fig. 10 shows a photoluminescence measurement result of the obtained crystal at a room temperature.

5 A sharp light emission peak corresponding to a band edge emission of undoped GaN was observed at 360 nm. It was also confirmed by the photo luminescence measurement that the obtained crystal is a high-quality GaN crystal.

10

(Embodiment 9)

As a ninth embodiment of the invention, an apparatus as shown in Fig. 11 was manufactured. An example in which the GaN crystal was epitaxially grown

15 by using the apparatus will be described.

A quartz crucible 45 having the inner diameter of 70 mm and the height of 150 mm was housed in a graphite susceptor 44 and was installed in a stainless vessel 43. 3000g of a molten Ga 48 was charged into

20 the quartz crucible 45 and a c-face sapphire single crystal substrate (hereinbelow, called a sapphire substrate) of (25 mm × 25 mm) was attached to the end of a substrate supporting jig 47 and was immersed in the molten Ga 48. The sapphire substrate 49 was fixed

25 inclined from the horizontal line by a few degree in

the molten Ga 48. An ammonia gas introduction tube 41 made of quartz having an end bent in a J-letter shape was installed in the molten Ga 48. The end of the gas introduction tube 41 was fixed so as to be positioned

5   just below the lower end of the sapphire substrate 49. In such a state, the molten Ga 48 was heated by heaters 42 and was controlled to be 950°C by an output of a thermocouple 46. Subsequently, ammonia gas was introduced via the ammonia introduction tube 41 at a

10   ratio of 0.1 1/min into the molten Ga 48 for one hour. The introduced ammonia gas rose as bubbles in the melt. The number of bubbles per minute was about 200. The bubbles of the ammonia gas rose in the solution collide with the lower end of the sapphire substrate

15   49 and rose along the surface of the substrate. After that, the bubbles reached the surface of the molten Ga 48 and were exhausted to the outside of the vessel. The exhausted gas was treated by a wet scrubber and was released to the atmosphere.

20   The grown crystal was cooled and was taken out from the molten Ga 48 and the metal Ga adhered to the surface was cleaned by hydrochloric acid. As a result, a transparent crystal thin film having the thickness of about 4 μm was obtained on the sapphire substrate.

25   The obtained crystal was confirmed to be a GaN crystal

by the X-ray diffractometry. The full width at half

maximum (FWHM) of the X-ray diffraction peak was about

5 min.

Fig. 12 shows a photoluminescence measurement

5   result of the obtained crystal at a room temperature.

A sharp light emission peak corresponding to a band

edge emission of undoped GaN was observed at 360 nm

and it was confirmed that the obtained crystal was a

high-quality GaN crystal.

10   Since the nitride crystal growth temperature, the

atmosphere pressure during growth, the dose of the

material, and the like are different according to the

kind of the nitride to be grown and the kind of a

material to be used, they cannot be unconditionally

15   determined.

The reason why ammonia is chosen as a gas

containing nitrogen is because of a result in which

chemical activeness to some extent, safety and

economical efficiency are considered. Theoretically,

20   hydrazine gas, mono methyl hydrazine, and the like can

be also used. Those gases have a danger of explosion

much larger than that of ammonia.

The temperature of the Group III material during

the crystal growth is set to be lower than the melting

25   point of the nitride to be grown in order to prevent

decomposition or re-melt of the grown crystal.

(Modification)

Although the GaN crystal growth has been described
in the embodiment, the invention can be also applied
to crystal growth of InN, AlN, or AlGaN or GaInN as a
mixed crystal of InN and AlN. Further, by doping an
impurity element in the Group III melt or the gas
including nitrogen, a nitride crystal in which an
impurity is doped can be also grown.

As a gas including nitrogen, except for ammonia,
it can be considered to use hydrazine, mono methyl
hydrazine, or the like.

The shape of the end of the tube for introducing a
gas such as ammonia into the Group III solution can be
variously modified in order to control the size and
the number of bubbles of the gas in the solution. For
example, a plurality of nozzles of bubbles can be
formed at the end of the gas introduction tube or a
net can be provided at the end of the gas introduction
tube.

A modification in which a plurality of seed
crystals or substrate crystals are provided in the
Group III solution can be also considered.

Although only the crystal growth vessel showing

the point part of the invention has been described in
the embodiments shown in Figs. 1, 2, 8, 9, and 11, if
a system in which a mass flow controller for
regulating the flow of the gas and a temperature

5   controller which can automatically control the
temperature of a heater by a program are combined is
constructed, the crystal growth can be more easily
controlled.

The nitride crystal obtained by the invention can

10   be widely applied as a semiconductor material or a
luminescent material. Especially, a bulk single
crystal substrate of a nitride is optimum as a
substrate material when a blue laser diode is produced.

15   (Embodiment 10)
As another embodiment of the invention, an example
of growing a GaN crystal by using an apparatus of the
construction as shown in Fig. 13 will be described. In
the embodiment, a liquid encapsulating agent is used.

20   The apparatus is assembled in a water-cooled
chamber 102 made of stainless. A stand 109 is arranged
on the bottom face of the water-cooled chamber 102 and
a cylinder 107 is put on the stand 109. A heater 104
and a heat insulating material 108 are arranged around

25   the cylinder 107. A piston 103 is slidably fit into

the upper end of the cylinder 107. The piston 103 is
vertically moved by a push rod 101 connected to a
hydraulic cylinder (not shown), thereby enabling a
material 106 arranged in the cylinder 107 to be

5   pressurized. The cylinder 107, the piston 103, the
stand 109, the heater 104, and the insulating material
108 are made of a high purity graphite.

The cylinder 107 has the inner diameter of 10 mm
and the height of 60 mm. 10g of GaN crystal powders as

10   a material 106 produced by the injection method and 2g
of B_2O_3 as a liquid encapsulating agent 105 were
charged into the cylinder 107. Each of the GaN crystal
powders and B_2O_3 was sufficiently ground in a mortar to
reduce the grain size. When the GaN crystal powders

15   and B_2O_3 were charged into the cylinder 107, it was
arranged so that B_2O_3 surrounds the GaN crystal powders.
Since the volume of the powder material 106 increased,
it was difficult to charge all of the amount into the
cylinder 107. The material was, therefore, dividedly

20   charged a few times while compressing the material 106
by using the piston 103 during the charging of the
material.

The pressure in the chamber 102 of the apparatus
to which the material 106 was charged was reduced to 1

25   $\times 10^{-2}$ torr via a valve 110 for atmosphere gas

substitution and the powders of the material 106 were
degassed. In such a state, a pressure of 4 ton/cm^2 was
applied to the material by using the piston 103 and
the material was heated to 2200°C by using the heater

5   104. After the pressurization and heating was
performed to the material 106 for three hours, the
heater temperature was lowered at a ratio of 2°C/min to
600°C, the pressurization by the piston 103 is
cancelled, the temperature was further cooled to a

10   room temperature, and the sample was taken out.

A GaN single crystal having a large grain size
which seems to be obtained in such a manner that the
molten GaN was slowly solidified was formed in the
cylinder 107 which was taken out, a GaN polycrystal

15   layer containing the metal Ga was formed around the
GaN single crystal and a thin B$_2$O$_3$ film covered on the
whole surface. The GaN single grain is in a hexagon
column shape having the diameter of 7 mm and the
height of 16 mm.

20

(Embodiment 11)

As another embodiment of the invention, the
following GaN crystal was grown by using the same
apparatus as that of the eighth embodiment. The

25   embodiment also uses a liquid encapsulating agent.

The apparatus in which molten B_2O_3 was thinly applied to the inner wall of the cylinder 107 and end faces of the piston 103 and the stand 109 was prepared. 10g of the GaN powders produced by the injection

5 method and 0.5g of the metal Ga were heated to 30°C and mixed well in a state where Ga was fused. The mixture was compressed by a press to be preformed in a disk shape having the diameter of 9 mm and the height of 22 mm. The preformed material 106 was set in the cylinder

10 107 and was heated to 650°C in a nitrogen atmosphere to soften B_2O_3 as a liquid encapsulating agent 105. In such a state, a pressure of 4 ton/cm^2 was applied to the material 106 by using the piston 103. Further, the material was heated to 2200°C in this state and was

15 left for three hours. After that, the material was cooled in a manner similar to the eighth embodiment, thereby obtaining a GaN single crystal having a similar grain size as that of the eighth embodiment.

20 (Embodiment 12)

As another embodiment of the invention, the following GaN crystal was grown by using the same apparatus as that of the eighth embodiment. The embodiment also uses a liquid encapsulating agent.

25 10g of GaN crystal powders as a material 106

produced by the injection method and 2g of B_2O_3 as a
liquid encapsulating agent 105 were charged into the
cylinder 107. When the GaN crystal powders and B_2O_3 are
charged into the cylinder 107, it was arranged so that
5   B_2O_3 surrounds the GaN crystal powders.

The pressure in the chamber 102 of the apparatus
to which the material 106 was charged was reduced to 1
$\times 10^{-2}$ torr via the valve 110 for atmosphere gas
substitution and the powders of the material 106 were
10   degassed. In such a state, the pressure of 100 ton/cm^2
was applied to the material by using the piston 103
and the material was heated to 1900°C by using the
heater 104. After the material was left for 48 hours
while the pressurization and heating was performed to
15   the material, the heater temperature was lowered at a
ratio of 20°C/min to 600°C, the pressurization by the
piston 103 was cancelled, the temperature was further
cooled to a room temperature, and the sample was taken
out.

20   There were some GaN single crystals each having a
large grain size which seem to be obtained in such a
manner that the GaN crystal grains were grown in solid
phase. There was a polycrystal layer of GaN having a
relatively small grain size around the GaN single
25   crystals. Further, the whole outer face was covered by

a thin B_2O_3 film. The shapes of the GaN single crystals were various. The largest crystal has the diameter of 6 mm and the height of about 10 mm.

5   (Embodiment 13)

As another embodiment of the invention, the following GaN crystal was grown by using the same apparatus as that of the eighth embodiment. The embodiment also uses a liquid encapsulating agent.

10   10g of the GaN crystal powders as a material 106 produced by the injection method and 2g of B_2O_3 as the liquid encapsulating agent 105 were charged in the cylinder 107. When the GaN powders were charged to the cylinder 107, it was arranged so that B_2O_3 surrounds

15   the GaN powders.

The pressure in the water-cooling chamber 102 of the apparatus to which the material 106 was charged was reduced to 1×10^{-2} torr via the valve 110 for atmosphere gas substitution and the powders of the

20   material 106 were degassed. In such a state, a pressure of 10 ton/cm^2 was applied to the material by using the piston 103 and the material was heated to 2200°C by using the heater 104. After the material was pressurized and heated for three hours, the heater

25   temperature was decreased to 2000°C and the material

was left for 30 minutes. Further, a pressurization
load was reduced to 9.5 ton/cm^2, the heater temperature
was increased to 2100°C, and the material was left for
30 minutes. After that, the heater temperature was
5   decreased to 2000°C and the pressurization load was
increased to 10 ton/cm^2. The above cycle was repeated
five times, the heater temperature was decreased
finally to 600°C at a ratio of 2°C/min, the
pressurization by the piston was cancelled, the
10   temperature was further cooled to the room temperature,
and the sample was taken out.

A GaN single crystal having a large grain size
which seems to be obtained by slowly solidifying the
molten GaN was formed in the cylinder 107 that was
15   taken out, a small amount of GaN polycrystal layer
containing the metal Ga was formed around the GaN
single crystal and the whole surface was covered by a
thin B$_2$O$_3$ film. The GaN single grain is in a hexagon
column shape having the diameter of 8 mm and the
20   height of 18 mm.

(Embodiment 14)

As another embodiment of the invention, the
following GaN crystal was grown by using an apparatus
25   of the construction as shown in Fig. 14. The

embodiment also uses a liquid encapsulating agent.

The apparatus has substantially the same construction as that of the apparatus shown in Fig. 13 but is different in a point such that the heater for

5　heating the material is divided into an upper heater 113 and a lower heater 114 so that the material 106 has a temperature gradient in the vertical direction of the diagram. The stand 109 has a water-cool construction so that the material can easily have a

10　temperature gradient.

A GaN single crystal produced by a method similar to that of the foregoing embodiment was shaped and arranged as a seed crystal 111 on the bottom part of the cylinder 107 made of high- purity graphite. On

15　the seed crystal, 10g of GaN crystal powders produced by the injection method was put as a material 106. B_2O_3 as a liquid encapsulating agent 105 was arranged so as to surround the GaN seed crystal and the powder material.

20　The pressure in the chamber 102 of the apparatus to which the material 106 was charged was reduced to 1 $\times 10^{-2}$ torr via the valve 110 for atmosphere gas substitution and the powders of the material 106 were degassed. In such a state, a pressure of 10 ton/cm^2

25　was applied to the material by using the piston 103,

the upper part of the material was heated to 2200°C by using the heater 114, and the lower part of the material was heated to 2000°C by using the heater 113. After the material was left in such a state for three

5   hours until the material powders were completely dissolved, the temperatures of the upper and lower heaters were decreased to 1800°C and 1600°C at a ratio of 0.5°C/min and then decreased to 800°C and 600°C at a ratio of 10°C/min, respectively. The pressurization by

10   the piston was cancelled, the material was further cooled to a room temperature, and the sample was taken out.

A GaN single crystal having a large grain size which seems to be obtained by slowly solidifying the

15   dissolved GaN was formed in the cylinder 107 that was taken out, a small amount of GaN polycrystal layer containing the metal Ga was formed around the GaN single crystal and the whole surface was covered by a thin B_2O_3 film. The GaN single grain is in a column

20   shape having the diameter of 10 mm and the height of 20 mm.

In each of the embodiments 8 to 12, except for B_2O_3, KCl, and NaCl, $BaCl_2$, $CaCl_2$, or the like can be also used as a liquid encapsulating material.

25   Although the load application direction was

vertical in the foregoing embodiments, a modification
in which the load is applied in the horizontal
direction is also possible. Modifications in which a
resistance heating is changed to an induction heating

5   or the like as heating means or a plurality of heating
means are used to minutely set a temperature
distribution and a temperature control at the time of
crystal growth, and the like can be also considered.
The direction of the temperature gradient can be the

10   opposite direction or the horizontal direction. The
direction of the temperature gradient and the load
application direction are not always necessary to be
coincided.

15   (Embodiment 15)

As further another embodiment of the invention, an
example of growing the GaN crystal by using a system
having the construction as shown in Fig. 15 will be
described. The embodiment uses a flux.

20   In the system, a heat insulating material 122, a
heater 123, and a susceptor 124 which are made of a
high- purity graphite are housed in a water-cooled
high-pressure chamber 121 made of stainless.

On the bottom of a cylindrical pBN crucible 125

25   having the inner diameter of 50 mm and the height of

150 mm, a sapphire substrate on which GaN has been preliminarily epitaxial grown by MOCVD was arranged as a seed crystal 128. The sapphire substrate was fixed to the bottom of the crucible so as not to be floated

5   when a flux is charged.

15g of GaN powders synthesized by the injection method as a material 127 and 100g of a metal Ga as a flux were charged into the crucible. The GaN powders and the metal Ga were heated to 50°C and mixed well in

10   a state where the metal Ga melts so that the metal Ga covers the surface of each of the GaN powders.

The pressure in the furnace was increased to 20 MPa with a nitrogen gas by operating a valve 126. While keeping the pressure, the material 127 was

15   increased to 1600°C. The material 127 was held at 1600°C for three hours, the GaN powders were dissolved in the Ga flux, the material temperature was decreased to 800°C at a ratio of 1°C/min, and after that, the material was quenched, and the pressure was returned

20   to the atmospheric pressure.

When the sapphire substrate serving as the seed crystal 128 which was subjected to the above growth processes was taken out from the furnace and the adhered Ga was cleaned by hydrochloric acid, a GaN

25   single crystal having the thickness of about 1.3 mm

was grown on the sapphire substrate.

(Embodiment 16)

As another embodiment of the invention, an example
of growing a GaN crystal by using a system having the
construction as shown in Fig. 16 will be described.
The embodiment also uses the flux.

The construction of the system is substantially
the same as that of the system described in the
thirteenth embodiment but is different in a point that
three heaters of an upper heater 131, a middle heater
132, a lower heater 133 are used in stead of one
heater. The heaters independently control temperatures,
so that the material 127 can have a temperature
gradient in the vertical direction.

A GaN single crystal produced by the method of the
thirteenth embodiment was placed as a seed crystal 128
on the bottom of the crucible 125. The seed crystal
128 was fixed to the bottom of the crucible 125 so as
not to be floated when a flux is charged. 50g of GaN
powders as a material 137 and 100g of Ga and 20g of Bi
as a flux were charged into the crucible 125. The GaN
powders obtained by heating the metal Ga to 900°C in an
ammonia gas flow, reacting Ga with N, and removing
unreacted Ga by aqua regia were used.

The GaN powders and the flux were heated to 250°C in an Ar gas atmosphere and were mixed well in a state where the flux melted, so that the surface of each of the GaN powders was covered by the flux.

5   Subsequently, 15g of B_2O_3 as a liquid encapsulating agent 129 was put on the material 127 obtained by mixing the GaN powders and the flux. The crucible 125 in which the seed crystal 128, the material 127, and the liquid encapsulating agent 129 were charged in the

10 above manner was set in the furnace for growth. The valve 126 was operated to provide an Ar gas atmosphere. The material was once heated to 700°C to melt B_2O_3, the furnace was then vacuumized and such a state was held for a predetermined time. This work was done to take

15 out bubbles included in the flux when the GaN powders and the flux were mixed. More bubbles did not come out from B_2O_3 after about 45 minutes elapsed, so that the pressure in the furnace was increased to 20 MPa with the Ar gas. While keeping the pressure, heating was

20 started to the material 137.

It is controlled so that the temperature of the upper heater 131 was 1600°C, the temperature of the middle heater 132 was 1400°C, and the temperature of the lower heater 133 was 1200°C, which were left in

25 such a state for 96 hours.

In the main growth, GaN which melted in the high temperature part was diffused and supersaturated in the lower temperature part, and GaN was deposited on the seed crystal arranged in the lowest temperature

5   part. The reason why the growth time is longer than that of the embodiment 13 is because it takes time to diffuse the solute in the flux. The charged GaN powders did not melt in the flux in a lump. Although unsolved GaN powders existed in the flux during the

10   growth, since the GaN powders have the density lower than that of the flux, the GaN powders were floated in the upper part of the flux and did not exert an adverse influence on the crystal growth on the seed crystal.

15   After such a state was left for 96 hours, each of the heater temperatures was reduced at a ratio of 5°C/min for three hours, and then the material was quenched. The pressure was returned to the atmospheric pressure.

20   When the seed crystal 128 subjected to the above growth processes was taken out from the furnace and the adhered flux was cleaned by aqua regia, a GaN single crystal having the thickness of about 4 mm was grown on the seed crystal.

25

(Embodiment 17)

As another embodiment of the invention, an example of growing a GaN crystal by using a system having the construction as shown in Fig. 17 will be described.

5 The embodiment also uses the flux.

The system is assembled in a water-cooled chamber 141 made of stainless. A stand 145 was installed on the bottom face of the water-cooled chamber 141 and a cylinder 151 is arranged on the stand 145. An upper

10 heater 144, a lower heater 143, and an insulating material 142 are installed around the cylinder 151. A piston 150 is slidably fit into the upper end of the cylinder 151. The piston 150 is moved vertically by a push rod 149 connected to a hydraulic cylinder (not

15 shown) so as to pressurize a material 147 arranged in the cylinder 151. The cylinder 151, the piston 150, the upper heater 144, the lower heater 143, and the insulating material 142 are made in a high purity graphite. The stand 145 on which the cylinder 151 is

20 put is water-cooled by a water-cooling pipe 152, thereby enabling the set temperature in each of the heaters 143 and 144 to be changed and the temperature gradient in the vertical direction of the material 147 to be set.

25 A GaN single crystal having the diameter 10 mm and

the thickness of 0.5 mm was placed as a seed crystal
148 on the bottom of the cylinder 151 having the inner
diameter of 10 mm and the height of 60 mm. 15g of a
mixture of the GaN powders synthesized by the

5   injection method and a metal Ga and 10g of a metal Ga
as a flux were charged in the cylinder 151. Since the
mixture of the GaN powders synthesized by the
injection method and the metal Ga can be obtained as a
mixture from the beginning, it saves the trouble of

10   mixing the GaN powders with Ga. It is difficult to
accurately obtain the amount of the GaN powders
included in the mixture. The amount of the GaN powders
included in the mixture charged this time was
estimated from the result of an analysis of a sampled

15   mixture as about 5g.

The pressure in the water-cooled chamber 141 in
which the material was charged was reduced to 1×10^{-2}
torr via a valve 146 for atmospheric gas substitution
and the bubbles of gas mixed in the material 147 were

20   taken out. In such a state, a pressure of 10 ton/cm^2
was applied to the material by using the piston 150,
the upper heater 144 was heated to 2200°C and the lower
heater 143 was heated to 1800°C. It was calculated
that the temperature in the upper part of the material

25   147 was about 2100°C and the temperature in the lower

part was 1900°C. After the material 147 was

pressurized and heated for three hours, the upper

heater temperature was decreased to 800°C and the lower

heater temperature was decreased to 600°C at a ratio of

5   2°C/min, the pressurization by the piston 150 was

cancelled, further the temperature was decreased to a

room temperature, and the sample was taken out.

In the cylinder which was taken out, there was a

GaN single crystal having a large grain size which

10   seemed to be obtained in such a manner that the molten

GaN slowly solidified and a metal Ga layer containing

a small amount of the GaN powders surrounded the

crystal. The GaN single crystal grain has a column

shape in which the central part is bulged. The

15   diameter was 10 mm and the maximum height was 11 mm.

The crystal growing method of the embodiment can

be also applied for growth of not only GaN but also a

nitride crystal except for GaN, for example, AlN or

InN or a mixed crystal of them. In this case, although

20   the kind of a flux which can be used and the growth

temperature may be different, they are substantially

the same as those in case of GaN.

As a liquid encapsulating agent 129, except for

B_2O_3, NaCl, KCl, $BaCl_2$, $CaCl_2$ or the like can be used.

25   The heaters 131, 132, 133, 143, and 144 as heating

means of the material 147 of a resistance heating type,
an induction heating type, a radiation heating type,
or the like can be used.

According to the invention as mentioned above,
5   excellent effects as shown below can be obtained.

(1) According to the fabricating method described
in claim 1 and 2, the gas containing nitrogen is
injected into the Group III melt at a temperature much
lower than the melting point of a nitride to be
10   synthesized, the liquid-phase Group III element and
the vapor-phase Group V element are reacted with each
other, and a solid-phase Group III nitride crystal is
directly formed in the Group III element melt. A large
amount of crystals can be therefore fabricated easier
15   and cheaper by a simple system in a shorter time as
compared with a case where a nitride melt is made.

(2) With respect to the mixture of the Group III
nitride microcrystal and the Group III metal material
according to claim 3 of the invention, since the
20   nitride microcrystal is synthesized in the Group III
melt, the surface of the nitride microcrystal is
completely covered with the Group III metal material.
When the mixture is used as a liquid phase growth
material, the mixture is very easily dissolved and the
25   saturated solution can be easily obtained as compared

with a conventional material. Consequently, the
controllability and reproducibility of the epitaxial
growth are largely improved.

(3) According to the growth methods of claims 4,
6, and 7 of the invention, a large quantity of the
high-impurity Group III nitride semiconductor crystals
can be produced easily and cheaply in a short time.
The method is safe since a gas such as hydrochloric
acid which is conventionally used in HVPE or a
dangerous material such as organic metal used in MOVPE
are unnecessary. According to the growth method of the
invention, a liquid phase growth or a vapor phase
growth of a nitride crystal which are especially
conventionally difficult can be easily performed. As a
result, a device having a p-type crystal of a high
carrier concentration can be easily produced without
performing any special process to a nitride crystal.
Since it is unnecessary to arrange the p-type
conductive layer on the surface of a device, the
degree of freedom in designing a device construction
is higher.

(4) In the nitride growing method according to
claims 4, 6, and 7 of the invention, since an oxide or
chloride which is conventionally used is not used as a
material, an unreacted substance does not become an

impurity when a liquid phase is grown. Consequently,
the mixture can be directly used as a material of the
liquid phase growth without extracting only a group
III nitride. Since the extraction process can be

5   omitted, not only the process can be largely shortened,
but also contamination of the material which tends to
occur in the extracting process can be eliminated, so
that the high-impurity liquid phase growth can be
realized.

10   (5) Further, according to the fabricating method
of the claims 8 and 9 of the invention, a Group III
nitride semiconductor crystal, especially, a bulk
single crystal which cannot be conventionally grown
can be grown. When the crystal is used as a substrate,

15   it is not only effective on higher efficiency and
longer life of a blue LED but also largely contributes
to promote a practical use of a blue LD which has not
been practically used. Such a Group III nitride
semiconductor crystal can be easily and cheaply grown

20   by a simple apparatus. In addition, it is unnecessary
to use a gas such as chlorine which is conventionally
used in HVPE or a dangerous material such as an
organic metal used in MOVPE, so that the method is
safe.

25   According to the nitride crystal growing method of

any one of the claims 11 to 27, a bulk crystal of a group III nitride compound (for example, GaN) which is conventionally almost impossible to produce can be produced by a simple method.

5   Since a hot press system which is available on the market and is widely used for forming ceramics or the like or an LEC which is generally used for growing a semiconductor crystal can be employed as an apparatus of the invention, a special apparatus is unnecessary

10   and the apparatus used for the invention is not so dangerous.

It is economical since only a small amount of the liquid encapsulating agent or the flux is necessary except for the material. Especially, in the method of

15   using the flux, since the flux can be repeatedly used, it is especially economical.

By using the nitride crystal obtained by the invention as a substrate crystal, not only the high efficiency and long life of a nitride LED can be

20   achieved but also an effect to promote practical use of a nitride LD which is not yet practically used can be expected.

25

CLAIMS

1. A nitride crystal growth method comprising a step of charging nitride crystal powders and a liquid encapsulating material into a cylinder and heating the materials while pressurizing by a piston.

2. The nitride crystal growth method according to claim 1, wherein a nitride melt is produced and after that, the pressure and the temperature are returned to a normal pressure and a room temperature, and the nitride melt is solidified.

3. The nitride crystal growth method according to claim 1, wherein the materials are heated until just before the nitride crystal powders melt and the nitride crystal is grown in a solid phase state.

4. The nitride crystal growth method according to any one of claims 1 to 3, wherein said nitride crystal powders are preliminarily formed under pressure.

5. The nitride crystal growth method according to claim 4, wherein a component element of the nitride crystal is used as a binder when the nitride crystal powders are formed under pressure.

6. The nitride crystal growth method according to claim 4, wherein the starting material of said nitride is Group III nitride crystal powders obtained by removing the Group III metal material from the mixture obtained by a nitride crystal fabricating method

comprising the steps of heating a Group III metal element so as to melt it, injecting a gas containing nitrogen atoms into the melt of the Group III metal element at a temperature lower than the melting point

5   of a nitride to be obtained, and obtaining a Group III nitride microcrystal in the melt of the Group III metal element.

7.   The nitride crystal growth method according to any one of claims 1 to 3, wherein material powders are

10   put in vacuum or a nitride atmosphere until at least the liquid encapsulating material melts.

8.   The nitride crystal growth method according to any one of claims 1 to 3, wherein the nitride material in the cylinder has a temperature gradient.

15   9.   The nitride crystal growth method according to claim 8, wherein a seed crystal is arranged on a low temperature side in the nitride material.

10.   The nitride crystal growth method according to any one of claims 1 to 3, wherein the pressure increase

20   and decrease and/or the temperature increase and decrease are repeated during crystal growth.

11.   A nitride crystal fabrication or growth method, substantially as any herein described in the Examples or with reference to the accompanying drawings.

25   12.   A nitride crystal produced by a method according to any one of the preceding claims.